

UNITED STATES PATENT OFFICE.

REEVE P. WALLIS, OF OAKLAND, CALIFORNIA.

FLEXIBLE LEAD-PENCIL.

SPECIFICATION forming part of Letters Patent No. 337,466, dated March 9, 1886.

Application filed July 31, 1885. Serial No. 173,177. (No specimens.)

To all whom it may concern:

Be it known that I, REEVE P. WALLIS, a resident of Oakland, Alameda county, State of California, have invented a new and useful Elastic Composition for Pencils; and I hereby declare that the following is a full, clear, and exact description of the same.

My invention relates to a composition having an elastic quality for forming pencils and pencil-points suitable for writing and drawing. Pencils made out of my composition are more certain and durable than those made out of the ordinary graphite, or a mixture thereof with clay and iron.

The following description fully explains the nature of my said invention and the manner in which I proceed to form and use the same for the purposes for which it is designed.

In order to get a composition which will have an elastic quality, and at the same time give distinct lines and marks with facility, I employ certain proportions of graphite and caoutchouc. After careful preparation these fundamental ingredients are intimately mixed by trituration, after which the mass is subjected to pressure and rolled into sheets of varying thickness. The sheets are cut to any desired size as to length and thickness, and the pieces inclosed in wooden cases, in the same way as the common pencils. The wood casing may have any usual form—as round or flat, octagonal or convexed. This latter form is adapted for carpentry and the shop gener-

ally, and the pencils made for these uses are strong and of extreme length. The elastic composition may be used also for pencil-points in short pieces to be inserted in pencil-cases made of metal or other material.

The proportions of the ingredients forming the elastic composition are varied to give the desired texture, and to produce degrees of hard and soft pencils adapted to the purposes of the desk, the drawing-table, and the work-bench.

I claim that the elastic quality of my compound gives a more certain and durable pencil-point. It is not friable and liable to crumble in the act of writing or pointing, and the point will not break because of a slight blow or a fall from desk or bench, and it is economical as well as useful.

Having thus fully described my invention, what I claim, and desire to secure by Letters Patent, is—

An elastic composition formed of certain proportions of graphite and caoutchouc, for pencils incased in wood, and for pencil-points to be used in cases of metal or other material, substantially as hereinbefore described and set forth.

In testimony whereof I have hereunto set my hand.

REEVE P. WALLIS.

Witnesses:

A. B. SMITH,
S. JOHNSON.

UNITED STATES PATENT OFFICE

2,280,988

PENCIL COMPOSITION

Mary Louise Weiser, Los Angeles, Calif., assignor
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a corporation of California

No Drawing. Application November 14, 1939,
Serial No. 304,388

4 Claims. (Cl. 106—19)

The present invention relates to novel mediums for use by artists and others, the mediums being preferably in the form of pencils or crayons adapted to mark objects made from derivatives of cellulose. More specifically stated, the invention pertains to compositions for use in pencils and the like, such pencils being capable of marking sheets of cellulose nitrate, cellulose acetate, etc., such compositions being particularly well adapted for use in drawing upon such sheets in colors whereby the sheets may be suitably superimposed and then photographed in colors in the production of photoplays, animated cartoons, etc.

Although the compositions embraced by the present invention may be used in the manufacture of various pencils and crayons capable of being employed in many diverse manners, the description appearing hereafter will be particularly directed toward compositions for use in the animated cartoon industry. In producing animated cartoons, particularly when the final films are to be in substantially natural color, the drawings originally made by the animators or artists are traced upon sheets of Celluloid and the outlines then filled in with suitable opaque paints. These sheets of Celluloid are called "cells" and the cells are placed in superimposed relation, each cell containing one or more elements or characters appearing in the final or completed scene. The cells may be placed in juxtaposition or may be spaced from each other but at all events the cells are photographed simultaneously, the opaque portions of foreground cells blocking out and covering portions of cells which are more distant from the camera.

In a co-pending application reference has been made to a technique of creating a depth of tone, which technique includes the steps of applying a stipple or shade or modifying tone to certain of the objects or characters depicted on the cells. The present invention is directed to pencil compositions which not only permit the artist to work directly on the cells but in addition permit the artist to produce pastel effects, textures, stipples and stains capable of creating the depth or roundness referred to in the co-pending application Serial No. 305,480 (Patent No. 2,254,462).

It is to be remembered that the cells are made from hard-surfaced materials such as organic plastics or resins (polymers of acrylic acid and vinyl acetate are examples) or comprise a derivative of cellulose, such as for example, cellulose nitrate or cellulose acetate. The cells are trans-

parent and provided with a glossy, substantially impervious surface having a very high surface tension particularly in comparison with normal ingredients, paints and the like. Hard wax pencils are incapable of leaving a uniform mark on these cells because of the peculiar characteristics of the surface of the cells. The compositions of the present invention, however, will produce smooth, uniform lines or if desired, the composition may be caused to result in a salebrous, irregular coating or mark closely simulating a spatter brush or stipple effect.

In a still further modification of the present invention the composition may contain a solvent capable of reacting with the cell surface so as to permit the excess material to be wiped off the cell and still leave a residual color or tone whereby translucent and semi-transparent shades or tone elements may be formed on the cell for the purpose of modifying underlying objects or colors. These stain or blend effects are of special utility when it is desired to impart roundness or depth to objects delineated upon the cells.

The compositions of the present invention comprise a base and suitable dyes and pigments. The base consists of waxes, binders and solvents and may also include plasticizing ingredients. The proportions of the ingredients employed may vary somewhat with the use to which the final composition is to be put and the effect desired.

An object of the present invention, therefore, is to disclose and provide a new medium with which artists and animators may express themselves on cellulose films, such as cellulose nitrate or cellulose acetate or on other transparencies.

Another object is to disclose and provide a novel composition of matter adapted for use in sketching or painting on transparent glossy materials such as sheets of cellulose derivatives or transparent plastics.

An object of the invention is to provide a waxy composition adapted for use in pencils, said composition containing solvents adapted to react with the surface of cellulose derivatives to which it is applied and to leave a dye or color tone thereon.

A further object is to disclose ingredients and compositions which result in a stable, effective art medium for use on cellulose derivatives, etc.

A still further object is to disclose binders, solvents and compositions for use in combination with waxes whereby pencils of novel characteristics may be produced.

These and other objects, uses, advantages and modifications of the invention will become apparent to those skilled in the art from the fol-

lowing detailed description of certain preferred ingredients and examples.

In making up the pencil compositions, various insect, vegetable and semi-mineral waxes may be used. The most commonly employed waxes are beeswax, candelilla, carnauba, Japan and montan wax. Stearin is also employed.

None of these waxes alone is capable of being used, however, since it will not adhere to a cell and does not have sufficient strength to retain its shape when in use. For example, beeswax, although capable of leaving a mark on a cell surface, will not make a continuous mark and is too flaky. Carnauba wax, although appreciably harder than beeswax, is too brittle and does not adhere well to the cell surface.

In accordance with the present invention it has been discovered that the waxes can be strengthened and their adherence to a cell surface markedly increased by including binders in the composition. The term "binder" as used herein refers to substances which are compatible with waxes and which have a tendency to hold the wax structure together. For example, ethyl cellulose is a relatively soft but tough substance soluble to some extent in stearic acid. Phenolic resins of various types may be used instead of ethyl cellulose. The binders not only assist in imparting strength to the compositions but have a tendency to raise the melting point thereof. Since many of the waxes employed are coarsely crystalline or have a tendency to cool into a coarsely crystalline structure, it is desirable to employ in the final composition a substance capable of inhibiting large crystal growth, thereby assuring the production of a pencil of more uniform and homogeneous character. Many of the waxes, such as for example, Japan wax, candelilla, carnauba, beeswax and montan wax, contain saponifiable constituents in various proportions and these constituents may be saponified or converted into soaps, in part at least, by the addition of a suitable mild base or alkali to the composition. Instead of employing ordinary caustic soda or potash, it has been found desirable to use a milder base such as triethanolamine or other similar amines.

When the final composition is to be used in a pencil capable of leaving a stain or dye on the cell surface, the pencil should contain a reagent capable of affecting the surface of the cell. Although many reagents or solvents answering this description are available (ketones, aryl halides, acetals, esters containing less than ten carbon atoms, etc.), I have found acetates such as carbitol acetate, phenol acetate, butyl acetate and ethyl acetate to be more desirable. Most of the solvents capable of rapidly reacting with the cell surface are relatively volatile and therefore the pencil compositions change in their properties and effectiveness, with age and storage. In order to stabilize the pencils, I have found it desirable to employ plasticizers, particularly those having some solvent effect or those which are capable of combining with the more volatile solvents without destroying the solvent effect thereof. For example, it has been found that dibutyl phthalate is an effective plasticizer for use in compositions of the character claimed herein since it is miscible with carbitol acetate and the like and instead of decreasing the solvent action of the acetate, appears to enhance the solvent effect. Other plasticizers such as octyl alcohol or linseed oil, may be used. Any soaps which may be formed by the addition of organic bases, such as tri-

ethanolamine, to the mixture during compounding may also be said to exert a plasticizing effect upon the composition.

Generally stated, it has been found that suitable pencils capable of being used in depositing a stain or tone upon a cell surface may be made from the following ingredients in the proportions given:

	General range	Preferred range
	Percent	Percent
Hard waxes.....	35 to 65	45 to 65
Soft waxes.....	0 to 40	5 to 25
Total waxes.....	50 to 80	65 to 80
Binders.....	4 to 15	4 to 15
Solvents.....	4 to 25	4 to 20
Plasticizers.....	0 to 15	5 to 15

In the event triethanolamine is used in the composition the products of reaction between the triethanolamine and any added fatty acid (such as stearin or fatty acids present in the waxes) may be considered to act not only as a means for inhibiting large crystal growth but also as a plasticizer. When such soap reaction products are present and are considered to act as plasticizers, then the total amount of plasticizers present may amount to as much as 25% to even 30%.

As has been stated before, the binders preferably comprise substances such as ethyl cellulose, resins and vegetable gums. In addition, highly polymerized oil products, varnish gums, thickened wood oil, etc., may be used.

It is to be understood that in addition to the above, suitable dyes (preferably oil soluble) either alone or in conjunction with pigments or pigments alone may be added to the base composition given for the purpose of imparting to the base composition a desired shade or tone. The percentage of dye and/or pigment by weight of the base may vary from about 0.5% to as high as 120%, depending entirely upon the tinctorial power of the dye or pigment employed and the shade or tone desired. Ordinarily, pigments of low specific gravity are to be preferred to pigments of high specific gravity since the latter do not appear to produce as homogeneous compositions and have a tendency to impair the ability of the composition to delineate a smooth, continuous, sharp line upon the surface of the cell.

The mode of compounding the ingredients comprises melting desired waxes in desired proportions and adding thereto with accompanying agitation the remaining ingredients of the mixture. Ordinarily the ingredients are maintained in molten condition for a period of from 15 minutes to several hours whereupon the pigments or dyes are added and the agitation continued while a temperature sufficient to produce a mobile mass is maintained. In the event the composition is to contain relatively volatile solvents, the solvents are added at as low a temperature of the mass as it is possible to maintain and still obtain homogeneous distribution of the solvent within the mass. When carbitol acetate, dibutyl phthalate are employed, these two ingredients are preferably premixed before being added to the warm wax base. After incorporating the ingredients in the manner stated, the mass is permitted to cool and is then formed into cylinders or rods, either by casting or by extruding the still plastic mass through suitable dies. The resulting cylinders or formed masses may be wrapped or encased in paper, wood or any other suitable composition.

Specific examples of compositions made in accordance with this invention will now be given:

	Percent	Percent	Percent
Montan wax.....	20	0	0
Candelilla.....	20	30	18
Carnauba.....	22	29	0
Japan.....	0	0	18
Stearic acid.....	10	9	37
Triethanolamine.....	5	5	0
Phenolic resin.....	5	5	0
Ethyl cellulose.....	0	1	11
Gum damar.....	0	5	0
Dibutyl phthalate.....	13	11	5
Carbitol acetate.....	5	5	11

It is to be remembered that suitable dyes, pigments or mixtures thereof are added to each of the bases. Oil-soluble dyes are preferably used.

It is further to be remembered that in the event it is desired that the pencil apply or form a smooth mark upon the surface to be treated, the quantity of binder be reduced somewhat or maintained at a minimum consistent with suitable strength of the composition. In some instances it is possible to eliminate the binder entirely. By using binders in amounts placing it within the upper end of the range indicated, a stipple-like effect is obtained when the pencil composition is applied to a sheet of nitrated cellulose or the like. Furthermore, when it is desired to produce a smooth pencil, larger quantities of so-called softer waxes are employed and smaller proportions of harder waxes. By soft waxes, reference is made to waxes such as bees-wax, stearin, etc.

I claim:

1. A pencil composition adapted to form a difficulty removable stain on the surface of objects made of cellulose derivatives, which comprises: a base containing 50% to 80% by weight of waxes,

from about 4% to 25% by weight of solvent capable of reacting with the surface of an object made of cellulose derivatives up to about 30% by weight of plasticizing agents, and a binder.

2. A pencil composition adapted to form a difficulty removable stain on the surface of objects made of cellulose derivatives and organic plastics, which comprises: a base containing 50% to 80% by weight of waxes, from about 4% to 25% by weight of solvent capable of reacting with the surface of an object made of cellulose derivatives and organic plastics up to about 30% by weight of plasticizing agents, a part at least of said plasticizing agents comprising products of reaction between an organic base and fatty acids, a binder, and an oil-soluble dye.

3. A pencil composition adapted to form a difficulty removable stain on the surface of objects made of cellulose derivatives and organic plastics, which comprises: a base containing 50% to 80% by weight of waxes, from about 4% to 25% by weight of solvent capable of reacting with the surface of an object made of cellulose derivatives and organic plastics, up to about 30% by weight of plasticizing agents, a part at least of said plasticizing agents comprising products of reaction between an organic base and fatty acids, 2% to 15% by weight of a binder, and an oil-soluble dye.

4. A pencil composition adapted to form a difficulty removable stain on the surface of objects made of cellulose derivatives and organic plastics which comprises: a base containing 50% to 90% by weight of waxes, up to about 30% by weight of plasticizing agents, a binder, a solvent capable of reacting with the surface of an object made of cellulose derivatives and organic plastics, and an oil-soluble dye.

MARY LOUISE WEISER.

UNITED STATES PATENT OFFICE

2,380,126

MARKING CRAYON

Fred A. Sturm, Paterson, N. J.

No Drawing. Application September 11, 1941,
Serial No. 410,373

7 Claims. (Cl. 260—738)

The present invention relates to a marking crayon, and it particularly relates to a marking crayon for textile use which will leave a substantially indelible mark resistant to dilute acids or alkalis, and which will substantially retain its original color, resisting any covering by dyestuffs during the dyeing process, whether acid or neutral, ranging in temperature from the atmospheric to prolonged boiling temperatures.

Considerable difficulty has been experienced in marking textile fabrics, particularly where such fabrics are not in completely finished state and must be subjected to treating baths of an acid or alkali nature since such markings even though indelible frequently will run or fade or be slightly destroyed by the acid or alkali, or other chemicals, or even hot or boiling water as the case may be.

It is among the objects of the present invention to provide an improved marking crayon particularly adapted for textile utilization, but also having wider application which will enable ready marking of textile fabrics in the greige or unfinished state, and before washing or treatment with alkaline or acid fluids and which will assure a substantially permanent durable marking thereon.

Another object is to provide an improved crayon composition which may be widely utilized to produce permanent markings which will not readily wear away or be destroyed by weather, wearing, or treatment with usual chemicals.

Other objects and advantages will appear from the more detailed description set forth below; it being understood, however, that this more detailed description is given by way of illustration since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the invention.

In accomplishing the above objects it has been found most desirable to form the crayon of a dispersed resin particles or globules carrying pigment and also if desired a plasticizer or softener, which particles or globules are suspended in or distributed through or surrounded by a continuous phase of wax having sufficient consistency to leave a film upon the fabric or other surface to be marked and which at the same time will not soften under summer temperatures nor become too rigid during the winter, and which will not be affected by humidity or dampness.

It has been found most suitable according to one embodiment of the present invention to provide a dispersion of a pigment in a resin which is resistant to dilute acid and dilute alkali such for example as chlorinated rubber, polymerized di-olefines, such as butadiene, balata or gutta percha. In the preferred form each pigment particle is distributed in the resin and may be coated by the resin so as to be resistant to acid or alkali,

these resinous materials having the coating so thin as not to affect the brilliancy of the pigment particle, but at the same time so that the pigment particle is completely coated by the resinous material. The pigments may be ground into the resin in liquid or paste form, or dispersed in the liquid resin, either in molten condition or in solution in an organic volatile solvent, such as acetone.

These resin coated pigment particles may then be suspended in desired proportions or formed with desired proportions with a body of wax. The proportions being so regulated as to give the desired rigidity and strength and also to permit a satisfactory detachment of a film of sufficient thickness when the crayon is drawn over a surface.

Although the rubber-like resinous materials are preferred, it is also possible to use in lieu of or in addition thereto similar acid or alkali resistant synthetic plastics or resins, such as acrylic resins, styrene resin, vinylite resins, urea-formaldehyde, alkyd resins, phenol-formaldehyde, coumarone resin, or analogous substances such as ethyl cellulose, cellulose nitrate, cellulose acetate, etc.

Among the waxes which may be utilized are carnauba, beeswax, candelilla wax, paraffin, montan wax, stearic acid, ceresin, spermaceti, Japan wax, tallow, hydrogenated oils, high melting point cocoanut stearins, ozokerite, etc.

Among the various pigments which have been found satisfactory to be incorporated in the resin and to be coated by the resin, preferably before incorporation in the wax are cadmium red or yellow, chrome yellow, chrome green, titanium white, iron oxide red, barium sulphate, zinc sulphide, red lead, basic lead sulphate, Prussian blue, burnt amber, yellow ochre, organic lacs, i. e. precipitated organic dyes, powdered aluminum hydrate and carbon black or desired combinations thereof. It is also desirable to use oil soluble or dispersible dyes. In some instances it is possible to use colored resins which will act as the coloring material.

Desirably, the resin is plasticized by a high boiling point solvent, such as diethyl phthalate, ethyl or butyl lactate, ethyl or butyl abietate, tri-phenyl or tri-cresyl phosphate, etc., so that the particles thereof will smear smoothly upon the surface and will form a thin film. The entire composition should be adjusted that the mark when made will dry promptly if not already dry when applied.

It has been found that the wax may range from 20% to 70% of the composition, the wax being proportioned so as to regulate the brittleness, elasticity and tendency toward oxidation of the composition.

Various composite waxes may be utilized such as Japan wax, and ozokerite with or without addition of spermaceti, etc. Petrolatum or a mineral oil may also be included to soften the composition. Drying or non-drying oils, fats, and waxes such as rapeseed oil, linseed oil, lithographic varnish tung oil, China-wood oil, and turpentine may also be introduced to give the desired consistency.

Desirably, the above compositions are mixed by melting them or by use of volatile organic solvents. In one process the pigment is stirred into the molten resin or resin and wax which is then solidified and cast or cut or formed into crayon sticks or rods ready for use.

To give another example, with a volatile solvent, 5 parts by weight of pigment may be mixed with 10 parts by weight of the resin itself in a volatile solvent such as naphtha or acetone together with $\frac{1}{20}$ to 1.10 parts of a plasticizer and $\frac{1}{20}$ to $\frac{1}{10}$ part of a stabilizer, and after the solvent has been evaporated forming a coating upon the particles, the mixture may then be combined with say 10 parts of a wax composition of equal parts of weight of beeswax and spermaceti.

The amount of resin in the final composition may vary widely and for example the resin may constitute as much as 20% to 50% of the final composition, with the pigment consisting of 5% to 20% of the composition, the balance being wax.

As still another composition the pigment may be dispersed by stirring in a volatile organic solvent containing from 10% to 15% of a high boiling point solvent and then into the solvent may be dissolved from 10 to 20 parts of a wax, and from 10 to 30 parts of a rubber-like resin as above stated. When the volatile solvent has been removed the final composition may be then worked into wax sticks useful as crayon, and the resin and wax composition be regulated so as to give the final product the advantage of hardness and weather-resistant properties.

As a further example there may be used the following compositions:

Carnauba wax	-----pounds	10
Barium sulphate	-----do	10
Cadmium selenide	-----do	9
Coumarone resin	-----do	10
Diethyl lactate	-----ounces	2

The resin and wax are melted together or the resin is dissolved in a solvent and then the barium sulphate and cadmium selenide are stirred in. The diethyl lactate is added at any state.

Soap, sodium lauryl sulphate, triethanolamine linoleate, mono or di-glyceryl stearates, palmitates or oleates may also be added in amounts varying from 1% to 5% as homogenizing agents.

Glue, casein, gelatin, molasses, gums, such as gum arabic or tragacanth, pectin, dextrin, starch, etc., may also be included in small amounts ranging from 2% to 8%.

Fillers, such as clay or kaolin, calcium carbonate, chalk, whiting, kieselguhr, diatomaceous earth, barium sulphate, talc, soapstone, etc., may also be included.

If desired, instead of, or in lieu of the waxes or wax to make the crayons softer or more smearable, it would be possible to use wax-like resins or gums, or to use such resins with other resins to give the desired composition which will be markable yet not too soft on one hand and not to brittle or hard on the other hand.

As further examples of compositions which may be employed:

Example IV

	Parts by weight
5 Coumarone resin	----- 16
Rubber chloride (Tornesit)	----- 12
Blown rapeseed oil	----- 12
Beeswax	----- 35
Paraffin	----- 25
10 Ethyl cellulose	----- 12
Triethanol linoleate	----- 10
Solvent (bityl carbitol)	----- 15
Ethyl lactate	----- 2
Ultramarine blue	----- 5

Example V

	Parts by weight
Phenol-formaldehyde (Amberol)	----- 25
Polybutene polymer (Vistanex)	----- 25
Beeswax	----- 40
20 Carnauba wax	----- 50
Castor oil	----- 5
Lithographic varnish	----- 10
Cobalt drier	----- 2
Ethyl acetate	----- 2
25 Soap (emulsifying agent)	----- 4
Cadmium yellow	----- 20
Tricresyl phosphate	----- 5

Example VI

	Indelible
30 Stearic acid	----- 10
Paraffin	----- 10
Coumarone resin	----- 20
Carnauba	----- 3
35 Beeswax	----- 5
Induline blue base	----- 3

Example VII

Pyroxilin lacquer	----- 10
Ethyl oleate	----- 10
40 Sodium oleate	----- 5
Carnauba wax	----- 20
Beeswax	----- 10
Chlorinated naphthalene	----- 15
Toluol	----- 5
45 Victoria blue B dye	----- 15

Example VIII

	Parts by weight
Urea-formaldehyde resin	----- 40
50 Isobutanol	----- 20
Bronze powder	----- 12
Polymerized vinyl acetate	----- 20
Carnauba wax	----- 20
Paraffin	----- 25
55 Ethyl abietate	----- 15
Turpentine	----- 5

If desired, after the crayon has been utilized to make a mark upon the fabric or textile material a hot iron may be run over the textile to cause the wax or resin to melt onto or into, or to form a better union with the textile fibers.

Desirably, after the wax has been removed either prior to the time the fabric is subjected to the action of dyeing and finishing bath or during the subsection of the fabric to dyeing and finishing baths, the resins should firmly adhere to the textile fibers causing permanent adherence of the pigments thereto so that the mark which is formed is a permanent mark and will not be removed by boiling nor will it be covered by dye baths, even though the dyeing solution be boiled for long periods of time as is customary in many forms of wool dyeing.

Where it is desired to have the resin harden or dry upon the textile fibers, a drying oil or a dry-

ing oil acid may be incorporated in the resin as for example in an alkyd resin embodying linoleic acid or linolenic acid or eleostearic acid. The wax compositions and ingredients acting as a vehicle for the pigment and resin should always be so adjusted that the crayon will leave a film of desired thickness upon the fabrics, and a desirably low melting point wax, such as paraffin, and high melting point wax, such as carnauba wax should be used to achieve the desired mixture. The resin or cellulose derivative should not be antagonistic to the wax and desirably adhere permanently to the textile fabric holding the dye or pigment in permanent position thereon, even though the wax be melted away from the resin or pigment or be removed by the hot washing or treating liquids. Where the resin in the wax does not readily mix in molten condition, a better mixture may be prepared by adding a small amount of an emulsifying agent, such as triethanolamine stearate or oleate, or sodium lauryl sulphate which will assure a better combination or emulsification of the resin in the wax. Lecithin may also be used for this purpose.

It will be noted, that the application above identified by the above composition has achieved a crayon which although it readily smears upon a textile fabric to form a marking thereon, will nevertheless form a permanent marking due to the action of the resin in holding the pigment firmly onto the textile fabric so that the color of the mark cannot be removed in prolonged treatment of dye baths even where the dyeing baths have contrasting colors which would ordinarily mask the color of the crayon. For example, where a yellow mark is placed upon the bottom edge of a woolen fabric which is then subjected to prolonged boiling in a dye bath to dye the fabric either a dark blue or black, the yellow color will remain intact, and after the finishing has been completed the only convenient way to remove such mark is to cut off the yellow end. In this manner assurance can be had that the fabric will be marked from the greige state all the way down to the finished material. These markings can be depended upon to supply an identification of the piece throughout the textile operations thereon, whether in wet or dry condition.

The present invention eliminates the necessity of using viscous, slow drying markings which must be permitted to dry and harden upon the fabric before the fabric can be subjected to any processing, and which cannot be readily handled in a textile plant since they frequently require the use of expensive collapsible metal tubes.

It is to be understood that the invention is not intended to be restricted to any particular composition or proportions, or to any particular application, or to any specific manner of use or to any of the various details thereof, herein described, as the same may be modified in various particulars or be applied in many varied relations without departing from the spirit and scope of the claimed invention, the practical embodiments herein described merely showing some of the various features entering into the application of the invention.

What is claimed is:

1. A marking crayon for textiles undergoing processing comprising a composition containing pigment, a chlorinated rubber, a high boiling plasticizer solvent and a wax, said pigment being dispersed in said composition and coated by said

chlorinated rubber and said wax preponderating over the chlorinated rubber content, said crayon forming a mark upon a textile which will remain thereon without substantial removal and masking even though the fabric be subjected to prolonged boiling treatments in finishing and dyeing baths, in the acid or alkali baths, and said marking resulting in an attachment of the pigment to the textile by the chlorinated rubber after removal of the wax, which chlorinated rubber not only serves as a permanent adhesive attachment to the pigment but also protects the pigment against masking from any chemical.

2. A marking crayon for marking textiles undergoing processing, comprising a composition containing a resin from the group consisting of acid, alkali and both acid and alkali resistant resins, a wax material, and a pigmenting substance, said pigmenting substance being incorporated in said resin, the proportion of said wax material being between 20 and 70% of the crayon composition.

3. A marking crayon comprising a resin from the group consisting of acid, alkali, and both acid and alkali resistant resins, a coloring substance, and a wax, said coloring substance being admixed with and incorporated in said resin acting as a coating for said coloring substance, said wax being a vehicle for said mixture of resin and coloring substance and adapted to provide requisite crayon marking properties, the proportion of said wax being at least equal to the resin content.

4. A marking crayon for marking textiles undergoing processing comprising a resin from the group consisting of acid, alkali, and both acid and alkali resistant resins, a pigment, a wax, and at least one substance from the group consisting of plasticizers, softeners, and homogenizing substances adapted to provide the crayon composition with predetermined marking characteristics for textile materials, said pigment being substantially dispersed within said resin and coated thereby, and said wax being a vehicle for said mixture of resin and pigment and in an amount at least equal to the resin content.

5. A marking crayon comprising an acid and alkali resistant resin, pigmentary particles homogeneously admixed with and coated by said resin, a wax in sufficient quantity to provide a vehicle for said resin and pigment mixture and in an amount at least equal to said resin, and at least one substance from the group consisting of plasticizers, softeners, and homogenizing substances adapted to provide the crayon composition with predetermined marking characteristics for textile materials.

6. A marking crayon comprising an acid and alkali resistant resin, a coloring substance intimately associated with and coated by said resin, and a vehicle for the resin and pigment comprising a wax having predetermined marking characteristics, the proportion of said wax being at least equal to the resin content.

7. A marking crayon comprising an acid and alkali resistant resin, coloring particles intimately admixed with and coated by said resin, and a vehicle for the resin and pigment comprising a wax having predetermined marking characteristics for textile materials, said resin content being in the proportion of 20-50% of the composition, said pigment in the proportion of 5-20%, and said wax in the proportion of 20-70% and at least equal to the resin content.

FRED A. STURM.

UNITED STATES PATENT OFFICE

2,396,219

LUMINESCENT MARKING MATERIAL

Lawrence T. Weagle, Oakmont, Pa., assignor to
Radio Corporation of America, a corporation of
Delaware

No Drawing. Application November 26, 1942,
Serial No. 467,055

1 Claim. (Cl. 252—301.4)

My invention relates to luminescent marking materials, to their method of manufacture and more particularly to such materials incorporating luminescent sulphides.

Luminescent materials, particularly of the sulphide type such as zinc and cadmium sulphides, deteriorate very rapidly upon exposure at atmospheric conditions. While the exact decomposition reactions are not known, the decomposition is believed to be a photolytic process initiated by ultra violet light and continued as an electrolytic process in an adsorbed film of normal atmospheric moisture. The result of the decomposition is a blackening or darkening of the sulphide and it has been found that a specimen of zinc sulphide which is subjected to damp air will darken and lose its luminescent properties thousands of times more rapidly than a specimen which is placed in a desiccator. For example, a specimen of zinc sulphide wherein a portion of the zinc has been displaced with cadmium to form zinc-cadmium sulphide activated by copper and used as a luminescent material in an evacuated lamp shows appreciably no darkening following 2000 hours of exposure to ultra violet rays, whereas an identical specimen placed in air saturated with moisture becomes very dark and loses a great degree of its luminescence in one-half hour. Consequently, luminescent materials of the sulphide type, while ideally suitable for marking material use from the fluorescent and phosphorescent aspects, are subject to rapid deterioration.

Objects of my invention are to provide a stable base or carrier for luminescent marking materials; to provide a diluent for luminescent materials, particularly of the sulphide type, which acts simultaneously as a carrier and as a decomposition inhibiting means; to provide a luminescent sulphide containing marking material which is inherently stable when subjected to moisture, ultra violet light and atmospheric conditions in general; to provide a carrier for luminescent sulphides whereby the chain or electrolytic action which favors further decomposition of the sulphide is interrupted, and to provide a low-cost method of manufacturing luminescent marking materials which when subjected to normal atmospheric conditions are highly stable. These and other objects, features and advantages of my invention will be apparent when taken in connection with the following description inasmuch as a drawing is believed unnecessary for a full and complete understanding of my invention.

In accordance with my invention, I provide a carrier or base of hygroscopic material, and pref-

erably incorporating a binder, with which the luminescent material is mechanically admixed, the mixture then being molded in any desired form for use as a marking means. Thus I have found, in accordance with my invention, that a material such as hemihydrated calcium sulphate having hygroscopic properties protects the luminescent material against darkening and consequent loss of luminescent properties. While I do not wish to be limited to any particular theory explaining this improved result, it is believed that the hygroscopic character of the hygroscopic material absorbs moisture and thereby fixes the moisture so that it has little or no effect upon the luminescent material associated with the hygroscopic carrier or diluent. I prefer to provide an aqueous mixture of the luminescent material with the hemihydrated calcium sulphate either with or without a water soluble binder such as polyvinyl alcohol which is then quickly formed into the desired shape so that it may set as a solid. During the setting process a portion of the hemihydrated material is converted to the dihydrated form which is in turn partially reconverted to the hemihydrated form by a baking or drying step. This may explain certain of the beneficial properties of my marking material in that it appears that even when only a minor portion of the material is hemihydrated the material has a greater affinity for atmospheric moisture which would otherwise cause deterioration of the luminescent material. Consequently, it would appear that when exposed to atmospheric conditions any water vapor present is bound by the calcium sulphate, rendering it ineffective in darkening or decomposing the sulphide luminescent material. Calcium sulphate is not greatly hygroscopic with respect to atmospheric moisture but rather hygroscopic to moisture from the luminescent material. It appears that such a material provides an interfacial absorption of the adsorbed moisture of the phosphor which is greater than the normal absorption of the moisture of the atmosphere. Consequently, excessive moisture is not drawn from the atmosphere by the desiccant. Thus any desiccant having a greater affinity for the adsorbed moisture of the luminescent material than that of the material for atmospheric moisture is suitable for practicing my invention. Such characteristics are possessed by calcium sulphate and calcium and magnesium carbonate and appear to be due to an interfacial phenomena occasioned by the proximity of the desiccant to, and the low surface tension of the moisture on, the luminescent material since moisture with the photolytic de-

composition products has lower surface tension than pure water.

As a particular example in practicing my invention, I dry-mix a small quantity of the hemihydrated calcium sulphate with a larger quantity of finely divided or crystalline luminescent material such as 20 parts of the hemihydrate with 80 parts of the luminescent material by weight. I then dissolve, preferably in a separate container from that containing the dry-mix, a small amount of water-soluble binder such as medium viscosity polyvinyl alcohol. The polyvinyl alcohol may be 2 parts to 98 parts water by weight. Other water-soluble or water-dispersible binders may be used such as dextrin or starch, although the percentage of such binding materials to the water is somewhat greater than that necessary with the polyvinyl alcohol binder, being from 5 to 10 per cent by weight. The purpose of this binder is to provide good adhesion both between the particles of luminescent material and between the particles of the desiccant, calcium sulphate. I have found that if such a binder is not used, the ratio of desiccant to luminescent material must be increased to a point at which the marking qualities of the product may be poor in that the material is too hard and the dilution too great for satisfactory use. Following the preparation of the dry-mix and the aqueous binder solution I dust a sufficient quantity of the dry-mix into the binder solution until the liquid is just absorbed. Following the dusting of the dry-mix into the binder solution I rapidly stir the materials to obtain a good mixture between the solid and liquid phase. Such stirring can be effected prior to the setting of the material, and I then immediately pour the mixed material into a positive mold. A further advantage of this method is that the mixture expands slightly upon setting and conforms to the outlines of the mold, providing a solid mass which is quite compact and smooth. After the mixture has set it is removed from the mold and dried at a relatively low temperature for a period of time such that a portion of the dihydrate reverts to the hemihydrate such as from 100 to 130° C.

I have found that less than 15 per cent of the desiccant such as calcium sulphate gives a friable product with insufficient strength for use as a marking material, whereas more than 30 per cent gives a product which is too hard for average use. I therefore prefer to use between 15 and

30 per cent of the hemihydrated calcium sulphate with respect to the total dry mixture of sulphate and luminescent material on a weight basis. In using other desiccants such as calcium or magnesium carbonate the preferred proportions are substantially the same as for calcium sulphate. The ratio of the dry-mix to the binder solution depends somewhat upon the particle size of the desiccant and luminescent material, although the procedure outlined above automatically compensates for these variables.

Various phosphors may be utilized in practicing my invention, the advantages thereof accruing especially in the use of zinc sulphide, cadmium sulphide and zinc-cadmium sulphide with or without the use of an activator such as silver, copper or gold. In addition, the particle size may vary over wide limits, being preferably less than 50 microns in diameter.

It will be appreciated from the above that I have provided a neutralizing ingredient homogenized with the luminescent material to assure stability during the time the marking material is subjected to atmospheric conditions whereby a high luminous efficiency of the material is assured until use. It will further be obvious that I have provided protection of the luminescent material from atmospheric moisture and human perspiration usually encountered during the use of such marking materials and that I have provided a mineral extender of low opacity to give good forming characteristics, adherence of the luminescent material to a writing surface, and a great reduction in cost both in the preparation and in the ingredients of my marking material. Thus while I have particularly pointed out the characteristics of my marking material constituents and their cooperative action, it will be appreciated that various equivalents may be used both in ingredients and mode of combination without departing from the spirit of my invention and the scope thereof as set forth in the appended claim.

I claim:

A soft friable luminescent marking crayon comprising approximately 20 parts of hemihydrated calcium sulphate and 80 parts of luminescent material of the sulphide type held together with a water-soluble binder.

LAWRENCE T. WEAGLE.

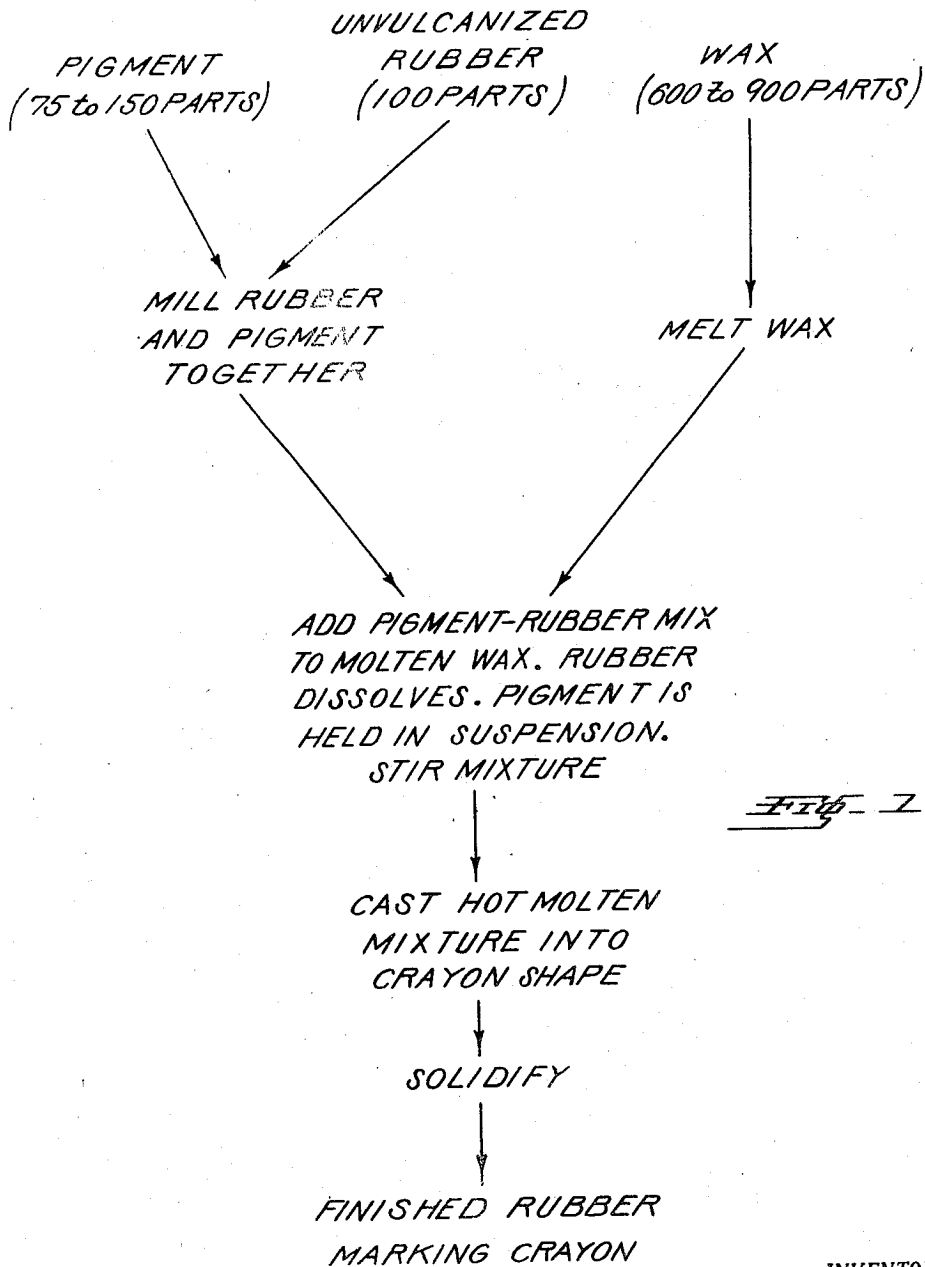
July 10, 1951

C. W. SMITH ET AL
COMPOSITION FOR MARKING RUBBER AND
METHOD OF USING COMPOSITION

2,560,195

Filed Nov. 7, 1947

2 Sheets-Sheet 1



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July 10, 1951

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2,560,195

Filed Nov. 7, 1947

2 Sheets-Sheet 2

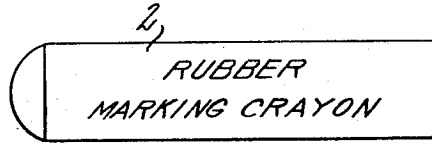


Fig-2

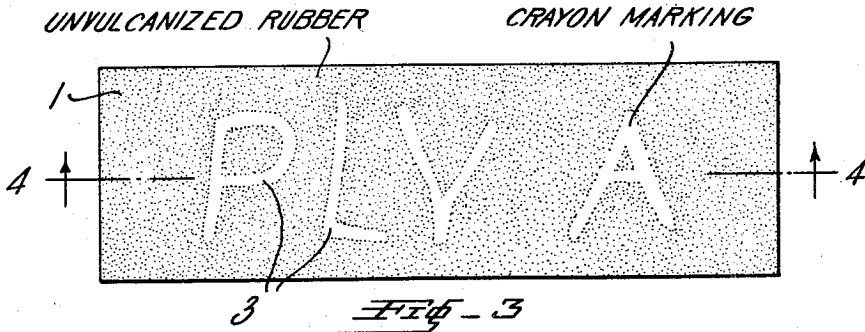


Fig-3

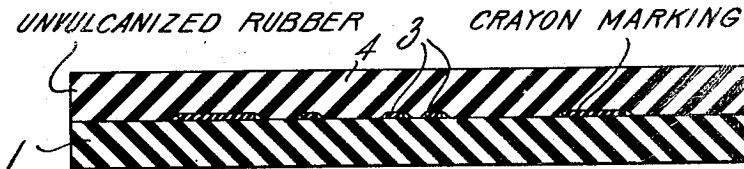


Fig-4

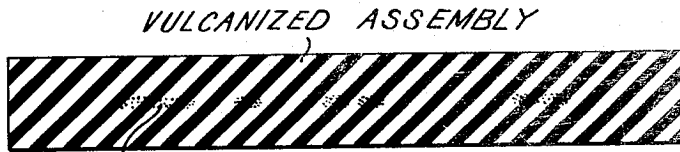


Fig-5

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UNITED STATES PATENT OFFICE

2,560,195

COMPOSITION FOR MARKING RUBBER AND METHOD OF USING COMPOSITION

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Application November 7, 1947, Serial No. 784,770

8 Claims. (Cl. 154—139)

1

This invention relates to marking of rubber surfaces. The invention particularly relates to a new composition of matter in crayon form for marking rubber. The invention accomplishes the marking of unvulcanized rubber surfaces without decreasing the adhesion to another rubber surface to be vulcanized thereto.

In the accompanying drawings,

Fig. 1 portrays diagrammatically the manufacture of a rubber marking crayon in accordance with our invention.

Fig. 2 portrays the finished crayon.

Figs. 3, 4, and 5 show the use of the crayon for marking a ply of unvulcanized rubber and bonding the marked ply to an unmarked ply of unvulcanized rubber, Fig. 3 being a plan view of a marked ply, Fig. 4 being a section of a plied-up assembly before vulcanization and Fig. 5 being a section of the vulcanized assembly.

It is often desirable to mark rubber surfaces. For example, in the manufacture of laminated rubber articles such as pneumatic tires, it is customary to mark all of the various plies of rubberized fabric, prior to plying them together and vulcanizing the assembly, with a crayon for identification purposes. Different colored crayons are employed for specific purposes.

Conventional crayons which are available consist of a wax with the proper color pigment in the wax. When these are used on unvulcanized rubber stock, the wax, being soluble in rubber, becomes diffused in the rubber, principally during cure, leaving the pigment remaining on the surface of the rubber. The pigment therefore is merely a dust which may be brushed off making identification difficult. When the pigment is interposed between two layers of rubber which are subsequently vulcanized the pigment acts as a lubricant or non-adherent foreign material which prevents adequate bonding of the rubber layers together.

We have found that rubber surfaces may be marked in a highly advantageous manner with a crayon formed from a mixture composed essentially of rubber, wax and pigment. The relative proportions of wax and rubber may vary from 600 to 900 parts of wax and from 75 to 150 parts of pigment per 100 parts of rubber.

We have found when rubber or rubberized stocks are marked with a crayon according to the

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present invention, that the marking is not only more permanent and readily visible but also does not interfere to an objectionable extent with the bonding of the marked rubber surface to another rubber surface to be vulcanized thereto. Thus even though the wax of the marking crayon of our invention dissolves in the rubber by diffusion at elevated temperatures such as those prevailing during curing it leaves the pigment on the surface intermixed with a rubber base as a binder. This binder prevents removal of the pigment from the surface by rubbing or abrasion because a rubber coating is formed around the pigment particles as in the case of a cement when the solvent evaporates. Ordinarily, a coating of a powder such as talc or the like will prevent adhesion between two rubber surfaces but that is not the case with the marking of our invention because of the effect just noted. As a result the bond obtained upon vulcanization of an assembly of two rubber surfaces with the marking of the present invention on one of the surfaces is in all cases very much stronger than it would be were the marking done with the conventional wax-pigment crayon.

The wax component may consist of a single wax or of a mixture of waxes. We may use any wax which when in the molten condition is a solvent for rubber, which is soluble in rubber and which yields a mixture having the necessary hardness and consistency to retain the shape of a crayon under conditions of marking. Examples of suitable waxes are: carnauba wax, paraffin wax, beeswax, mineral wax, ozocerite, montan wax, Japan wax, Chinese insect wax, candelilla wax, etc. We may also use artificial waxes such as those prepared by heating mixtures of higher acids and alcohols under esterifying conditions. We may also use higher fatty acids having the physical properties of waxes, especially stearic acid. We often prefer to use a blend of a major proportion of carnauba wax and a minor proportion of paraffin wax. In many cases we prefer to employ a minor proportion of stearic acid in the wax. For example we secure very good results by the use of a wax mixture composed of a major proportion of carnauba wax and minor proportions of paraffin wax and stearic acid. In addition to serving as a wax, stearic acid acts as a modifying agent in controlling the hardness char-

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acteristics of the crayon. Where several waxes are used, their proportions should be so adjusted as to give the desired hardness in the crayon.

We may use any pigment capable of imparting the desired color to the marking and sufficiently opaque that the mark is easily visible. Titanium dioxide is especially suitable but we may use other white pigments such as zinc oxide, barium sulfate, lithopone, etc. Where a colored marking is desired, we may use pigments having the desired color such as yellow, blue, green, red, orange, brown, black, etc. We often prefer to use titanium dioxide in conjunction with zinc oxide since zinc oxide is very beneficial in rubber stocks although it is not as white as titanium dioxide.

The proportions of rubber, wax and pigment may be varied within the limits stated above. The higher proportions of pigment are used where a particular vivid marking, such as one of white, is desired.

In preparing the material, the compounding may conveniently be accomplished by mixing the rubber and pigments on a mill and subsequently placing this compound mix into the hot molten wax whereupon the rubber dissolves and the pigments are held in suspension. The hot wax containing the dissolved rubber and suspended pigments is stirred and poured into molds to form the crayons. If desired, the mix may be allowed to solidify in bulk and at any subsequent time it may be heated and poured into molds. Fig. 1 of the drawings, which is self-explanatory, portrays the preferred way of making the crayons of our invention. Fig. 2 shows the finished crayon.

It is often desirable to incorporate a portion of the wax component, such as the stearic acid, with the rubber pigment mix for the purpose of softening the compound during the milling operation.

If desired, any of the conventional curing agents, such as sulfur, and accelerators may be added to the mix. For example, one part of mercaptobenzothiazole and three parts of sulfur per 100 parts of rubber may be used. In most cases, however, use of curing agents and of accelerators is unnecessary since there will be sufficient migratory accelerators and curing agents from the adjoining stocks to cure the rubber in the crayon deposited in marking. The present invention applies primarily to the marking of unvulcanized rubber, since that is the most extensively practiced, but it may advantageously be employed to mark vulcanized rubber surfaces because it leaves a more permanent mark even after the wax or waxes have dissolved in the rubber. The invention applies to either natural or synthetic rubber.

In using the crayon of our invention, a ply of unvulcanized rubber 1 is marked with the crayon 2 to give the marking 3. This marked ply is then placed adjacent a second ply 4 of unvulcanized rubber as shown in Fig. 4. It will be understood that the marking 3 is greatly exaggerated in thickness for purpose of illustration. The plied-up assembly is then vulcanized to give the integral assembly shown in Fig. 5. In Fig. 5, the particles 5 of pigment from the marking 3 are shown although it would be practically impossible to locate them in an actual vulcanized assembly because the amount of pigment deposited in a marking operation is extremely small. Since the residual pigment particles are completely surrounded by rubber, they do not weaken the bond obtained upon vulcanization.

Following are typical examples of crayon for-

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mulations in accordance with our invention. In each example, by "rubber" is meant natural rubber such as smoked sheets, although GR-S (butadiene-styrene rubbery copolymer) or other suitable synthetic rubber may be employed in place thereof. All parts are by weight.

Example 1

Rubber	100
Zinc oxide	10
Titanium dioxide	100
Stearic acid	150
Paraffin wax	150
Carnauba wax	500

Example 2

Rubber	100
Titanium dioxide	100
Paraffin wax	300
Carnauba wax	500

Example 3

Rubber	100
Zinc oxide	50
Titanium dioxide	50
Paraffin wax	800

Example 4

Rubber	100
Zinc oxide	10
Titanium dioxide	100
Green pigment	25
Stearic acid	100
Paraffin wax	100
Carnauba wax	500

The rubber and pigment were mixed together to a uniform mixture by milling on a rubber mill. The resulting mixture was then placed with stirring in the molten wax which was at a temperature slightly above its melting point whereupon the rubber dissolved and the pigment went into suspension. The hot mixture was stirred, poured into molds, and allowed to cool. The resulting crayons displayed excellent rubber marking characteristics. Examples 1 to 3 gave white crayons while Example 4 produced a green crayon.

From the foregoing description, many advantages of our invention will be readily apparent to those skilled in the art. Among these advantages are the cheapness and simplicity of manufacture of our rubber marking crayons, the distinctness and permanence of the markings produced therewith and the good adhesion between rubber surfaces vulcanized together with the marking therebetween in contrast to the greatly reduced adhesion caused by markings with conventional wax crayons.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. The method which comprises marking an unvulcanized rubber surface by rubbing said surface with a crayon composed of a stick of an unvulcanized normally solid marking composition consisting essentially of unvulcanized rubber, rubber-soluble wax and pigment, in proportions by weight of from 6 to 9 parts of said wax and from 0.75 to 1.5 parts of said pigment per part of rubber, said rubber being dissolved in said wax and said pigment being suspended in the resulting solution, placing another unvulcanized surface in contact with the marked surface and subsequently vulcanizing said rubber surfaces together, the bond produced therebetween by the vulcanization being much stronger than it would be if the marking were deposited

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from a conventional wax-pigment rubber marking crayon.

2. The method which comprises marking an unvulcanized rubber surface by rubbing said surface with a crayon composed of a stick of an unvulcanized normally solid marking composition consisting essentially of unvulcanized rubber, a wax mixture comprising a major proportion of carnauba wax and a minor proportion of paraffin wax, and pigment, in proportions by weight of from 6 to 9 parts of said wax and from 0.75 to 1.5 parts of said pigment per part of rubber, said rubber being dissolved in said wax and said pigment being suspended in the resulting solution, placing another unvulcanized surface in contact with the marked surface and subsequently vulcanizing said rubber surfaces together, the bond produced therebetween by the vulcanization being much stronger than it would be if the marking were deposited from a conventional wax-pigment rubber marking crayon.

3. The method which comprises marking an unvulcanized rubber surface by rubbing said surface with a crayon composed of a stick of an unvulcanized normally solid marking composition consisting essentially of unvulcanized rubber, a wax mixture composed of a major proportion of carnauba wax and minor proportions of paraffin wax and stearic acid, and pigment, in proportions by weight of from 6 to 9 parts of said wax and from 0.75 to 1.5 parts of said pigment per part of rubber, said rubber being dissolved in said wax and said pigment being suspended in the resulting solution, placing another unvulcanized surface in contact with the marked surface and subsequently vulcanizing said rubber surfaces together, the bond produced therebetween by the vulcanization being much stronger than it would be if the marking were deposited from a conventional wax-pigment rubber marking crayon.

4. A method as set forth in claim 1 wherein said composition forming said stick was prepared by milling said pigment and said unvulcanized rubber together and subsequently admixing the resulting pigment-rubber mixture with the hot molten wax.

5. As a new article of manufacture, a crayon for marking rubber, said crayon being composed of a stick of an unvulcanized normally solid composition consisting essentially of unvulcanized rubber selected from the group consisting of natural rubber and butadiene-styrene rubbery copolymer, rubber-soluble wax and pigment, in proportions by weight of from 6 to 9 parts of said wax and from 0.75 to 1.5 parts of said pigment per part of said rubber, said rubber being dissolved in said wax and said pigment being suspended in the resulting solution, said composition having such hardness and consistency that the crayon retains its shape under conditions of marking, whereby in the resulting deposited marking even though the wax diffuses into the rubber of the marked surface the pigment is left on the surface intermixed with the rubber of the marking so that removal of the marking from the marked rubber surface by rubbing or abrasion is prevented, and upon vulcanization of an assembly of another rubber surface with a rubber surface marked with said crayon, the bond obtained is much stronger than it would be if the marking were deposited from a conventional wax-pigment crayon.

6. As a new article of manufacture, a crayon for marking rubber, said crayon being composed

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of a stick of an unvulcanized normally solid composition consisting essentially of unvulcanized rubber selected from the group consisting of natural rubber and butadiene-styrene rubbery copolymer, a wax mixture comprising a major proportion of carnauba wax and a minor proportion of paraffin wax, and pigment, in proportions by weight of from 6 to 9 parts of said wax and from 0.75 to 1.5 parts of said pigment per part of said rubber, said rubber being dissolved in said wax and said pigment being suspended in the resulting solution, said composition having such hardness and consistency that the crayon retains its shape under conditions of marking, whereby in the resulting deposited marking even though the wax diffuses into the rubber of the marked surface the pigment is left on the surface intermixed with the rubber of the marking so that removal of the marking from the marked rubber surface by rubbing or abrasion is prevented, and upon vulcanization of an assembly of another rubber surface with a rubber surface marked with said crayon, the bond obtained is much stronger than it would be if the marking were deposited from a conventional wax-pigment crayon.

7. As a new article of manufacture, a crayon for marking rubber, said crayon being composed of a stick of an unvulcanized normally solid composition consisting essentially of unvulcanized rubber selected from the group consisting of natural rubber and butadiene-styrene rubbery copolymer, a wax mixture composed of a major portion of carnauba wax and minor proportions of paraffin wax and stearic acid, and pigment, in proportions by weight of from 6 to 9 parts of said wax and from 0.75 to 1.5 parts of said pigment per part of said rubber, said rubber being dissolved in said wax and said pigment being suspended in the resulting solution, said composition having such hardness and consistency that the crayon retains its shape under conditions of marking, whereby in the resulting deposited marking even though the wax diffuses into the rubber of the marked surface the pigment is left on the surface intermixed with the rubber of the marking so that removal of the marking from the marked rubber surface by rubbing or abrasion is prevented, and upon vulcanization of an assembly of another rubber surface with a rubber surface marked with said crayon, the bond obtained is much stronger than it would be if the marking were deposited from a conventional wax-pigment crayon.

8. A crayon for marking rubber, said crayon being composed of a stick of an unvulcanized normally solid composition consisting essentially of unvulcanized rubber selected from the group consisting of natural rubber and butadiene-styrene rubbery copolymer, rubber-soluble wax and pigment, in proportions by weight of from 6 to 9 parts of said wax and from 0.75 to 1.5 parts of said pigment per part of said rubber, said rubber being dissolved in said wax and said pigment being suspended in the resulting solution, said composition having been prepared by milling said pigment and said unvulcanized rubber together and subsequently admixing the resulting pigment-rubber mixture with the molten wax, said composition having such hardness and consistency that the crayon retains its shape under conditions of marking, whereby in the resulting deposited marking even though the wax diffuses into the rubber of the marked surface the pigment is left on the surface intermixed with the

rubber of the marking so that removal of the marking from the marked rubber surface by rubbing or abrasion is prevented, and upon vulcanization of an assembly of another rubber surface with a rubber surface marked with the said crayon, the bond obtained is much stronger than it would be if the marking were deposited from a conventional wax-pigment crayon.

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HAROLD GOLDEN.

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2,645,582

PENCIL LEAD

Georg Loy, Nurnberg, Germany, assignor to J. S. Staedtler, Mars-Bleistiftfabrik, Nurnberg, Germany, a corporation of Germany

No Drawing. Application January 16, 1950, Serial No. 138,930. In Germany October 14, 1949

4 Claims. (Cl. 106—19)

1

The object of this invention is unburned pencil leads the lines of which cannot be removed either mechanically (by erasing) or with the usual chemicals (diluted acid and alkaline fluids, oxidizing and reducing solutions and gases, organic solvents), nor fade under the influence of light.

Producing indelible writing by means of writing pencils was frustrated chiefly by the fact that the lines made by the leads stick only to the surface of the paper. When lines are made with indelible pencils, the aniline dye-stuff contained in the lead is being absorbed by the tissue of the paper under the influence of air moisture. It penetrates, however, not deeply into the paper. Besides, the aniline dye-stuff can be destroyed under the influence of chemicals so far as to form a colorless combination; nor are they constant against the influence of light.

Therefore, when producing leads which are to fulfill the purpose set forth above, such writing materials have to be used as do not possess the aforesaid unfavorable qualities. Under this aspect, especially soot must be considered, which is neither destructible by chemicals nor subject to the influence of light. The procedure heretofore known of adding soot to such masses out of which pencil leads are made was, however, not fitted for the present purpose nor was it suited for it, because it was not intended to add to the masses such materials as would enable the paper to be colored (blackened) by soot to the depth of its tissue.

This idea is the basis for the present invention. The results of numerous experiments have shown that soot, when applied in the finest colloid distribution, can be introduced into the interior structure of the paper tissue by using the capillary attraction of the paper tissue and will dye it black, provided that, to the mass mixed with soot, such materials will be added that will lower the surface tension of the boundary surface, soot+paper tissue, and therefore penetrate the paper surface adsorptively. Preferably such materials will be used the polar groups of which will support the activity of the surface, e. g. such materials with hydroxyl, carboxyl and sulphur groups. Also capillary attractive hydrocarbon compounds, as Vaseline, are well suited.

Upon writing, a greater amount of soot gathers at the border lines of the cellulose fibre roughened by writing and of the writing material delivered by the lead, whereby the carbon is absorbed by the paper tissue. It may be surmised that Van der Waal forces and Dipol forces are working as binding forces.

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The lead mass can be mixed with a dye-stuff resistable to the influence of chemicals; or the materials added for the purpose of reducing the surface tension can be dyed with such a material; so that the lines made with the lead can be copied. Colored leads produced in this way make lines which cannot be removed either mechanically or chemically and are constant against the influence of light, even on heavily glued paper.

Besides writing leads also drawing leads can be produced, making lines which, in contrast to drawings made with India ink, cannot be destroyed or removed.

In carrying out the said invention, a lead mass is produced which has e. g. the following substances:

Example I

15 parts soot and 15 parts graphite as writing materials,
30 parts talcum as filling and gliding material,
20 parts calcium stearate as gliding material,
10 parts glycerine as surface-active material,
20 parts tragacanth as binding material.

Example II

15 parts soot,
15 parts graphite,
20 parts talcum,
40 parts calcium stearate,
15 parts glycerine,
40 parts benzoyl cellulose and 55 parts vinyl acetate as binding materials.

Example III

15 parts soot,
15 parts graphite,
35 parts talcum,
35 parts calcium stearate,
15 parts Vaseline,
20 parts tragacanth.

The lead masses constituted according to the above examples can be mixed with a copying dye-stuff e. g. Methylene Blue and/or Sudan dyestuff, if leads are desired which can be copied.

The mass is kneaded, rolled, filtered, and pressed into leads in the known way. The leads readily formed do not change during the process of being burned.

Having thus described the invention, I claim as new and desire to secure by Letters Patent:

1. A pencil lead comprising about 15 parts soot, about 15 parts graphite, from 20 to 35 parts talcum, from 20 to 40 parts calcium stearate, from 20 to 40 parts gum tragacanth, and 10 to 15 parts Vaseline.

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2. A pencil lead comprising about 15 parts soot, about 15 parts graphite, about 30 parts talcum, about 20 parts calcium stearate, about 10 parts glycerine, and about 20 parts gum tragacanth.	Number	452,890
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3. A pencil lead comprising about 15 parts soot, about 15 parts graphite, about 35 parts talcum, about 35 parts calcium stearate, about 15 parts Vaseline, and about 20 parts gum tragacanth.	5	1,970,603
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4. A pencil lead comprising soot, graphite, talcum, calcium stearate, gum tragacanth, and a surface active agent.	10	

GEORG LOY.

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2,784,164

LEADS OR CRAYONS AND METHOD OF MAKING THE SAME

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10 Claims. (Cl. 260—15)

This invention relates to a lead or crayon rod which may be made in any desired length, shape or size, and as a pencil core or crayon rod and may have any desired color, including black and white. More particularly stated, the invention relates to leads or crayon rods of the non-calcined type.

It is well known that writing or marking materials of the non-calcined type are usually affected by changes in the relative humidity of the ambient atmosphere. An increase in the relative humidity causes an increase in diameter and an increase in flexibility, but a decrease in transverse strength and a softening of the mark made by the lead or crayon.

On the other hand, a decrease in the relative humidity of the surrounding atmosphere causes a decrease in diameter, a decrease in flexibility, an increase in transverse strength, and a hardening of the mark made by the lead or crayon. Changes in dimensions or diameter are particularly objectionable in small diameter mechanical pencil leads since an increase in diameter causes the leads to bind in the tip and a decrease may prevent a proper gripping of the lead in the pencil chuck.

This invention has for its salient object to overcome these difficulties and to provide a lead or crayon rod of the non-calcined type so constructed that it will not be deleteriously affected by variations in the relative humidity of the ambient atmosphere.

Another object of the invention is to provide a marking material that will have superior marking qualities under all atmospheric conditions.

Another object of the invention is to provide a lead or crayon of the non-calcined type so constructed and so treated that it will not absorb moisture.

Another object of the invention is to provide a method of rendering a water imbibing binder in a lead or crayon of marking material, insoluble in water.

Further objects will appear more fully from the following specification.

The ingredients of filler, color, waxy material and water imbibing agglutinant or binder may be conventional.

For instance, the filler may be talc, clay, pyrophyllite, etc. Any water or oil soluble dye or any pigment may be used.

The waxy material may be calcium stearate or any water insoluble metal soap which will withstand the heat of the heat treatment hereinafter explained.

Although methyl cellulose is recommended as the agglutinant or binder, the invention is not limited to this specific material, but the binder should be a water imbibing or hydrophilic material which will be rendered substantially unaffected by water or moisture by the addition of a melamine type resin or resin having like characteristics and a heat treatment hereinafter described. Other cellulose derivatives, particularly the lower alkyl ethers, that is, ethers of cellulose and lower molecular weight aliphatic acohols, may be used as the agglutinant or binder.

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A thermosetting melamine resin is preferably added, but any material may be used which, when added to a mixture constituted as above described, renders the binder substantially insoluble after heat treatment. Materials in addition to melamine resin that have this property are thermosetting resins, such as urea formaldehyde resins and resorcinol formaldehyde resins.

As an example of suitable ingredients for a lead or crayon having the desired characteristics, the following ingredients in the approximate proportions stated may be used.

	Percent
Talc or other filler.....	10-70
Color pigment or dyestuff.....	5-40
Calcium stearate (waxy material).....	5-40
Methyl cellulose (agglutinant or binder).....	2-15
Melamine-formaldehyde resin.....	1-8

The method of forming the leads or crayons is as follows: the agglutinant is wetted with sufficient water to form a paste and the wetted binder and other ingredients are given intensive mixing to form a homogeneous dispersed mixture.

It may be desirable to add a wetting agent for the purpose of lowering the surface tension to permit more intimate blending of the ingredients.

The mixture may then be passed through a three roll mill for additional dispersion.

The mixer is then preferably forced through a multiple hole die, forming strands, and the strands are then compressed into a compact mass. Then the mixture or mass is extruded to form leads or rods. The rods or leads are then oven dried at a temperature of approximately 170° F. to drive out all moisture therefrom.

Thereafter, the dry rods or leads are heated to approximately 250°-350° F. for about a three minute minimum, which treatment renders the composition and binder water insoluble. Reference to percent means parts per hundred, that is, percentage by weight.

Although one specific embodiment of the invention has been particularly described, no limitations are intended aside from those imposed by the appended claims.

What we claim is:

1. A method of making non-calcined water insoluble crayon and pencil leads unaffected by moisture, which comprises forming a paste of water and a water-absorbent lower alkyl ether of cellulose to provide a binder, mixing from about 2 to 15% of said cellulose ether binder with filler, coloring material, and a water insoluble metal soap capable of withstanding the temperatures of subsequent heat treatment, as the predominant constituents, and from about 1 to 8% of a thermosetting resin selected from the group consisting of melamine-formaldehyde, urea-formaldehyde and resorcinol-formaldehyde resins, forming the mixture into shaped leads, heating the shapes to remove moisture, and thereafter further heating the shapes to from about 250 to 350° F. to cure the resin and render the shapes water-insoluble and non-absorbent.

2. A method according to claim 1 in which the thermosetting resin is a melamine-formaldehyde resin.

3. A method according to claim 1 in which the alkyl cellulose ether binder is methyl cellulose.

4. A method of making non-calcined crayon and pencil leads comprising mixing 10-70% filler, 5-40% coloring material, 5-40% water insoluble metal soap, 2 to 15% of a water absorbent lower alkyl ether of cellulose as an agglutinant, and 1 to 8% of a thermosetting resin selected from the group consisting of melamine-formaldehyde, urea-formaldehyde and resorcinol-formaldehyde, forming the mixture into shaped leads, and heating the shapes to cure the resin and render the leads water insoluble and non-absorbent.

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5. A method according to claim 4 in which the water insoluble soap is calcium-stearate, and the agglutinant is methyl cellulose.

6. A non-calcined crayon or pencil lead comprising a heat treated shaped composition consisting essentially of a filler, coloring material, and a water insoluble metal soap in predominant amount, from about 2 to 15% of a water absorbent lower alkyl ether of cellulose as a binder, and from about 1 to 8% of a heat cured thermo-setting resin selected from the group consisting of melamine-formaldehyde, urea-formaldehyde, and resorcinol-formaldehyde resins imparting non-absorbent and water insoluble properties to said binder and composition.

7. An article according to claim 6 in which the alkyl cellulose ether binder is methyl cellulose.

8. An article according to claim 7 in which the water insoluble metal soap is calcium stearate.

9. An article according to claim 8 in which the resin is a melamine-formaldehyde resin.

10. A non-calcined crayon or pencil lead comprising a heat cured shaped composition which is non-absorbent to moisture and water insoluble consisting essentially of

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the following ingredients in the stated proportions, filler 10-70%, coloring material 5-40%, calcium stearate 5-40%, methyl cellulose 2-15%, and melamine-formaldehyde resin 1-8%.

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2,850,490

VULCANIZABLE AND VULCANIZED PRODUCTS FROM POLYETHYLENE AND PROCESS FOR THEIR PRODUCTION**Peter J. Canterino and Albert N. De Vault, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware****No Drawing. Application July 12, 1954
Serial No. 442,892****13 Claims. (Cl. 260—94.9)**

This invention relates to the halogenation and dehalogenation of hydrocarbon polymers. In one aspect it relates to a process for producing a vulcanizable polymeric material. In another aspect it relates to a novel vulcanized composition.

It is known in the art to produce solid polymers of ethylene and other olefins by polymerization of ethylene or other olefins at very high pressure in the presence of an oxygen-containing catalyst. It is also known in the art to halogenate and to dehalogenate such solid polymers, the halogenation and the dehalogenation being conducted as separate steps. Recently, it has been found that solid polymers of ethylene and other olefins can be produced at relatively low pressures by polymerizing ethylene or other olefins in the presence of a catalyst comprising chromium oxide, usually associated with another oxide. This process and the products thereof are described in the copending application of J. P. Hogan and R. L. Banks, Serial No. 333,576, filed January 27, 1953, now abandoned.

This invention provides a novel and improved process for halogenating and dehalogenating a polymer of an olefin to obtain a partially dehalogenated material which can be vulcanized to produce a novel composition. The vulcanized composition has many uses, some of which are specifically described herein.

According to this invention, there is provided a process whereby a polymer of an aliphatic olefin, e. g. ethylene, can be halogenated and at least partially dehalogenated in substantially a single step and in a single reaction zone to produce a vulcanizable product. The process is conducted by reacting the polymer, at a temperature above its melting point, with a halogenating agent under such conditions that halogenation and partial dehalogenation occur substantially simultaneously. This result is effected by conducting the reaction between the polymer and the halogenating agent at a temperature in the range 150–300° C., preferably 175–275° C. When the reaction is begun at a temperature in the lower part of the broad range of temperature, e. g. 150–175° C., it is preferred to raise the temperature to a value in the range 175–300° C. after substantial halogenation has occurred. It is often preferred to conduct the reaction in the range 175–300° C., in which range halogenation and at least partial dehalogenation occur without further adjustment of the temperature. The halogenation-dehalogenation reaction can be conducted in the presence of a dehydrohalogenation catalyst such as metallic magnesium, metallic zinc, magnesium chloride, zinc chloride or barium chloride. However, the reaction proceeds satisfactorily in the absence of a catalyst and it is, therefore, often preferred to conduct the reaction without a catalyst. The reaction can be conducted in the presence of a halogenation catalyst of the type known in the art or the reactants can be irradiated as, for example, with sunlight or ultraviolet light. It is ordinarily preferred to use irradiation because this manner of operation introduces no foreign materials into the reaction mixture.

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Alternatively, the reaction can be conducted in the absence of a halogenation catalyst. Although dehydrohalogenation appears to constitute a substantial part of the dehalogenation, the invention is not limited to such a reaction mechanism.

As the halogenating agent, an elemental halogen of the group chlorine, bromine, or iodine or a compound which yields these elements under the reaction conditions can be used. Examples of such halogen-yielding compounds or halogenating agents are carbon tetrachloride, carbon tetrabromide, carbon tetraiodide, hexachloroethane, chloroform, iodoform, bromoform, and phosgene.

The preferred polymer used as the starting material can be any normally solid or tacky polymer of an aliphatic olefin and ordinarily will be a normally solid polymer of a monoolefin such as ethylene, such polymers being produceable as previously described herein. The term "normally solid polymer of ethylene," as used herein, contemplates both homopolymers and copolymers of ethylene, such as copolymers of ethylene with propylene. Although a preferred polymer is a normally solid polymer of ethylene, viscous or semisolid polymers of olefins as disclosed in the cited application of Hogan and Banks can be used. Normally solid polymers of propylene, 1-butene, 1-pentene, or 1-hexene can also be used. A preferred type of polymer is one produced by polymerizing an aliphatic 1-olefin having a maximum chain length of 8 carbon atoms and no chain branching nearer the double bond than the 4-position in the presence of a chromium oxide polymerization catalyst as more fully disclosed in the cited application of Hogan and Banks.

Further, according to this invention, the product of the halogenation and partial dehalogenation can be vulcanized to produce novel materials which have a wide variety of uses. Thus, the vulcanized materials can be molded to form shaped articles, extruded to form pipes or tubes, extruded onto wire to form insulation therefor, or applied to various surfaces as coating materials or heat insulators. Also, in accordance with the invention, a pigment can be added to the recipe, prior to vulcanization, and in such a case a composition is obtained which, after vulcanization, is useful as a marking composition, useful, for example, in crayons, pencils and similar instruments. Suitable pigments which can be incorporated into the composition are carbon black, graphite, titanium dioxide, malachite and iron oxide. Other pigments known in the art can also be used to obtain the color desired. The amount of pigment added is generally within the range of 5 to 75 parts by weight per 100 parts by weight of the halogenated and partially dehalogenated polymer although larger or smaller quantities can be employed. A preferred range is 25 to 60 parts of pigment, and a more preferred range is from 40 to 60 parts. It will be understood by those skilled in the art that the optimum proportion of pigment will depend upon, among other things, the nature of the specific pigment used.

The term "vulcanization" as used herein is intended in the same general sense as that term is used in the rubber or elastomer art. Thus, the vulcanization ordinarily comprises heating the halogenated and partially dehalogenated polymer, for example at a temperature in the range 350–400° F., with a vulcanizing agent such as elemental sulfur, zinc oxide, magnesium oxide, or other known vulcanizing agent such as a suitable organic sulfur compound. Sulfur is the vulcanizing agent which is most widely used.

Vulcanized products ranging from flexible, leathery substances to hard plastics are obtained from solid polyethylene, according to this invention, by first treating the polymer with a halogen such as chlorine, bromine, or

iodine or a halogenated hydrocarbon such as carbon tetrachloride or hexachloroethane at an elevated temperature to obtain an unsaturated polymeric material which is then mixed with a vulcanizing agent, and such other compounding ingredients as desired, and vulcanized.

When treated in accordance with one manner of practicing this invention, a solid ethylene polymer is first melted, the temperature is adjusted to the desired level, e. g. 175–300° C., and the halogen or halogenated hydrocarbon is introduced while the reaction mixture is stirred to facilitate contact of the halogen with the polymer. While the scope of the invention is not dependent upon any particular reaction mechanism, it is believed that halogenation of the polyethylene first occurs, followed by dehydrohalogenation. The halogenating agent can be introduced throughout the entire reaction period or the addition of halogenating agent can be stopped and heating continued to effect further dehydrohalogenation. The type of product can be controlled by the amount of halogen introduced, the length of the heating period, if any, which follows, and the temperature. The reaction time will usually range from 1 to 30 hours but can be longer or shorter. The unsaturated polymer thus obtained is then mixed with a vulcanizing agent and such other compounding ingredients as desired such as activators, accelerators, fillers, etc., and the compounded stock is then vulcanized.

The production of the unsaturated polymers is effected essentially in one step, the only agent added being a halogen or a halogenated hydrocarbon, such as carbon tetrachloride or hexachloroethane. It is not necessary that a halogenation step be effected first in the presence of a solvent or dispersing medium followed by a separate dehydrohalogenation step in which a dehydrohalogenating agent is employed. By merely controlling the reaction conditions, a vulcanizable material is readily obtained in a single step.

Instead of operating at a high temperature throughout the reaction period, i. e., 175–300° C., it is sometimes preferred to use a lower temperature during the addition of the halogen or halogenated compound (carbon tetrachloride or hexachloroethane) and then to raise the temperature toward the end of the reaction period. For example, the halogen can be introduced into the melted polyethylene at a temperature below 175° C. and the temperature then raised and maintained at the higher level for the desired period.

The halogen or halogenated compound can be added over a period of from 1 to 10 hours and the mixture then heated, if desired, for a period up to 20 hours or longer. During the heating period, it is frequently preferred to flush the reactor with an inert gas such as carbon dioxide or nitrogen to purge the system of hydrogen halide which has been formed during the reaction. During the entire reaction period, i. e., during the addition of halogen and also during the heating period, the reaction mixture is stirred or otherwise agitated.

When chlorine, carbon tetrachloride, or hexachloroethane is employed, the amount preferred is generally in the range from 8 to 60 parts by weight per 100 parts polyethylene although larger quantities can be added if desired. With other halogens, corresponding amounts, based on the equivalent weights, are used. While the products frequently contain halogen, it is generally considered desirable, if the halogen is chlorine, that the halogen content not exceed 10 percent by weight and preferably that it be less than 7 percent by weight. A suitable range of chemically bound chlorine content is from 2 to 7 weight percent. Corresponding amounts of the other halogens can be present instead of chlorine.

This invention provides a method for obtaining polymeric materials ranging in unsaturation from 2 to 15 percent or higher (2 to 15 double bonds per 100 ethylene units in the polymer) from polyethylene. It is believed

that these unsaturated materials are free from cross linkages, i. e., the halogenation and dehydrohalogenation occur in the same polymer chain. These materials, when compounded and vulcanized, yield valuable products which range from flexible leathery substances to hard plastics, depending on the details of the method of preparation. The vulcanized products are much more solvent resistant than the polyethylene from which they were prepared and are also resistant to the action of acids and alkalis. The unvulcanized products have little strength and cannot be molded satisfactorily, while the vulcanized materials can be employed in the manufacture of various molded articles and can be extruded into pipe or onto wire as insulation. They can also be used as coating materials.

Example I

Ethylene was polymerized, over a chromium oxide-silica-alumina catalyst containing 2.4 weight percent chromium as chromium oxide operating at 320° F. and a pressure of 400 p. s. i. g., a space velocity (volumes liquid/volume reactor/hour) of 6, and a feed containing 3 weight percent ethylene is isooctane. The ethylene feed rate was 1.3 pounds/hour and the isooctane flow rate was 11 gallons/hour. The polyethylene obtained was insoluble in benzene and acetone. It had a molecular weight of 13,640.

One hundred fifty grams of the polyethylene described above was charged to a reactor provided with a stirrer and a Dry-Ice condenser. The polyethylene was melted, the temperature was adjusted to 160° C., and 66 grams of chlorine was introduced over a period of approximately four hours while the reaction mixture was stirred and irradiated with ultraviolet light. The temperature was maintained at 150–170° C. After introduction of the chlorine, stirring was continued and the mixture was heated to 250° C., over an 8-hour period to complete the dehydrochlorination. The reactor was flushed with carbon dioxide during the heating period to purge the system of HCl which was formed during the reaction. The product had a chlorine content of 5.05 weight percent and an unsaturation of 6.9 percent (an average of 6.9 double bonds per 100 ethylene units). Unsaturation was determined by the iodine monochloride titration method.

The unsaturated product was compounded in accordance with the following recipes:

	Parts by Weight	
	I	II
Unsaturated product from polyethylene chlorination and dechlorination.....	100	100
Stearic acid.....	2	2
Sulfur.....	2	2
Zinc oxide.....	5	5
Agerite Alba (hydroquinone monobenzyl ether).....	1	1
N,N-dimethyl-S-tert-butylsulfenyl dithiocarbamate.....	1.5	1.5
Carbon black (SAF black).....		50

The mixtures were milled on a hot mill and vulcanized by heating at 300° F. for 45 minutes. The samples were tested on an Instron tester using 0.2 inch cross-head speed. The following results were obtained:

Sample No.	Tensile, p. s. i.	Elongation, percent	Description of Product
I.....	1,090	92	Flexible, leathery product, insoluble in toluene.
II.....	1,065	4.5	Hard, somewhat brittle product, insoluble in toluene.

For control purposes an uncompounded sample of the unsaturated product was heated under the same conditions used for vulcanization of the compounded samples. A hard, crumbly material, soluble in toluene, was ob-

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tained. It could not be removed from the mold without breaking.

The vulcanized material containing carbon black (recipe II) marks on paper in much the same manner as an ordinary pencil. The marks do not smear and are easily erasable. Thus, it is evident that the vulcanized product of this invention can be used as a binder for graphite in the manufacture of pencils. Other types of carbon black, such as channel black, lamp black, acetylene black, high-abrasion furnace black, and the like, can be used as pigments. This type of product can be fabricated into leads for mechanical pencils.

Example II

A sample of polyethylene (400 grams) prepared as described in Example I, and having a molecular weight of 10,050 was charged to a reactor provided with a stirrer and a Dry-Ice condenser. The polyethylene was melted, the temperature was adjusted to 160° C., and 120 grams of chlorine was introduced over a period of approximately six hours. During the addition of the chlorine the temperature ranged from 150–170° C. The mixture was stirred throughout this period, and irradiated with ultraviolet light. Stirring was continued while the temperature was raised to 240–250° C. and the reactor was flushed with carbon dioxide as in Example I. The product has an unsaturation of 11.6 percent, as determined by the iodine monochloride titration method, and contained 3.88 weight percent chlorine.

A portion of the product was compounded in accordance with the following recipe:

	Parts by weight
Polymer	100
Stearic acid	2
Sulfur	2
Agerite alba (hydroquinone monobenzyl ether)	1
N,N-dimethyl-S-tert-butylsulfenyl dithiocarbamate	1.5
Zinc oxide	5

The sample was cured 45 minutes at 307° F., and physical properties were determined. Physical properties were also determined on a sample of chlorine-treated but un-compounded polyethylene and on the original polyethylene. The following results were obtained:

	Compounded and Vulcanized Sample	Uncompounded Sample	Original Polyethylene
Percent unsaturation	11.6	11.6	0.
Percent chlorine	3.88	3.88	0.
Compounded and vulcanized	Yes	No	No.
Tensile, p. s. l.	1,185	1,270	2,660.
Elongation, percent	45	15	10.
Softening point, ° F.	> 270	222	270.
Flex temperature, ° F.	-38	-36	Brittle.
Electrical properties:			
1 kc., ¹ —			
Dissipation factor	0.0032	0.0031	< 0.0005.
Dielectric constant	2.64	2.64	2.35.
1 mc., ² —			
Dissipation factor	0.0170	0.0160	< 0.0005
Dielectric constant	2.75	2.56	2.32.
Vol. percent swell in toluene:			
At 78° F.	37.2	Disintegrated.	Partially soluble.
At 212° F., 24 Hr.	124	Dissolved.	

¹ Rubbery product; does not lose its shape at 260° F.

² Kilocycle.

³ Megacycle.

The foregoing data show that a rubbery material having desirable electrical insulation properties and low solubility in toluene is prepared according to this invention.

Example III

A sample of commercial polyethylene¹ (400 grams) having a molecular weight of 11,500 was melted, the temperature was adjusted to 160° C. and 96 grams of chlorine

¹ Presumably prepared by polymerization in the presence of an organic peroxide-type catalyst at a pressure of the order of 5000–10,000 p. s. l.

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was introduced over a 6-hour period while the mixture was stirred and irradiated with ultraviolet light. The procedure was similar to that described in the preceding examples. During chlorination, the reaction mixture became very viscous. After addition of the chlorine, the mixture was heated to 240–250° C. and stirred while the reactor was flushed with carbon dioxide. The product had an unsaturation of 6.05 percent as determined by the iodine monochloride titration method, and contained 5.6 weight percent chlorine.

A portion of the product was compounded using the recipe given in Example II. The sample was cured 45 minutes at 307° F., and physical properties were determined. Physical properties were also determined on the treated but un-compounded product and on the original polyethylene. The following results were obtained:

	Compounded and Vulcanized Sample	Uncompounded Sample	Original Polyethylene
Percent unsaturation	6.05	6.05	0.
Percent chlorine	5.6	5.6	0.
Compounded and vulcanized	Yes	No	No.
Tensile, p. s. l.	595	495	830.
Elongation, percent	70	170	73.
Softening point, ° F.	189	180	212.
Flex temperature, ° F.	-52	-60	-40.
Electrical properties:			
1 kc., ¹ —			
Dissipation factor	0.0029	0.0034	< 0.0005.
Dielectric constant	3.05	2.86	2.3.
1 mc., ² —			
Dissipation factor	0.0268	0.0180	< 0.0005.
Dielectric constant	2.70	2.69	2.3.
Vol. percent swell in toluene at 78° F.	115.5	Disintegrated	Soluble.

¹ As in Example II.

The foregoing data show that useful products are obtained, according to this invention, from polyethylene other than those produced by polymerizing ethylene in the presence of a chromium oxide catalyst.

Example IV

Polyethylene was prepared in a manner similar to that described in Example I to give a product having a molecular weight of 9,000. To 130 grams of this material heated to 200° C., 30 grams of chlorine was introduced over a two-hour period while the mixture was stirred. The temperature increased to 230° C. and was maintained at this level during the reaction. The product contained 5.1 weight percent chlorine and had an unsaturation of 4 percent as determined by the iodine monochloride titration method. This product can be vulcanized according to the procedure in the foregoing examples.

Example V

Ten milliliters (16 grams) of carbon tetrachloride was added to 150 grams of the polyethylene described in Example IV and the mixture was heated to 180° C. At the end of this period, more carbon tetrachloride was introduced over a period of six hours until a total of 17 ml. (27 grams) had been added. Toward the end of the reaction the temperature increased to 210° C. The mixture was stirred throughout the reaction period. The product contained 2.8 weight percent chlorine and had an unsaturation of 5.2 percent as determined by the iodine monochloride titration method. This product can be vulcanized as previously described.

Example VI

One hundred fifty grams of polyethylene prepared as described in Example IV was heated to 190° C., and 60 grams of bromine was added dropwise over a period of four hours while the reaction mixture was stirred. The temperature was maintained at 190–210° C. throughout the reaction period. Heating and stirring were continued for 0.5 hour after addition of the bromine. The product contained 2.8 weight percent bromine and had an

unsaturation of 3.6 percent as determined by the iodine monochloride titration method. Infrared analysis on a sample which had been purified by crystallization from methylcyclohexane showed the product to be unsaturated. This product can be vulcanized as previously described.

The vulcanizable products of this invention generally contain from about 1 to about 10 weight percent, and frequently from 2 to 7 weight percent, chemically combined halogen, and have an unsaturation in the range 2 to 15 percent (average number of double bonds per monomer unit) and frequently 3 to 12 percent. However it is within the scope of the invention to effect substantially complete halogen removal especially where bromination and/or iodination agents are used.

The molecular weights mentioned herein are determined by the methods of Kemp and Peters, *Ind. Eng. Chem.* 35, 1108 (1943), and Dienes and Klemm, *J. App. Phys.* 17, 458-471 (June 1946).

The molecular weights were calculated according to the equation

$$M = \frac{4.03 \times 10^3 \times N_i \times 14}{1.303}$$

wherein M is the molecular weight and N_i is the intrinsic viscosity as determined for a solution of 0.2 gm. of polymer in 50 cc. of tetralin at 130° C.

While certain examples, process steps and compositions have been disclosed for purposes of illustration, the invention is clearly not limited thereto. The essence of the invention is that there is provided a process for the substantially simultaneous halogenation and partial dehalogenation of a polymer of an aliphatic olefin and that the process produces a vulcanizable composition, which, when vulcanized, yields a useful and novel vulcanizate. It will be evident to those skilled in the art that variation and modification within the scope of the disclosure and the claims can be practiced.

The foregoing examples and discussion relate primarily to batch-type operation. It should be understood that the same reactions can be carried out in a continuous manner, using suitable equipment, as will be evident, to those skilled in the art, from this disclosure.

We claim:

1. A process which comprises reacting a normally solid polymer of an aliphatic olefin with a halogenating agent at a temperature in the range of 150° C. to 300° C. for a period of 1 to 30 hours, effecting halogenation and at least partial dehalogenation with removal of hydrogen halide in substantially a single step, the dehalogenation being effected at a temperature of at least 175° C. and within said range, regulating reaction conditions of temperature and time to provide a product having an

unsaturation of from 2 to 15 percent and a combined halogen content not exceeding 10 percent by weight and recovering the resulting halogenated product.

2. The process of claim 1 in which the halogenation and dehalogenation are carried out in the temperature range of 175° C. to 300° C.

3. The process of claim 1 in which the normally solid polymer is a polymer of ethylene and the halogenating agent is selected from the group consisting of chlorine, bromine, iodine, and materials capable of yielding these halogens.

4. The process of claim 3 in which the halogenating agent is elemental chlorine.

5. The process of claim 3 in which the halogenating agent is added over a period in the range of 1 to 10 hours and heating is continued for an additional period up to 20 hours after introduction of the halogenating agent has ceased.

6. The process according to claim 5 wherein said halogenating agent is elemental chlorine.

7. The process according to claim 5 wherein said halogenating agent is elemental bromine.

8. The process according to claim 5 wherein said halogenating agent is elemental iodine.

9. The process according to claim 5 wherein said halogenating agent is carbon tetrachloride.

10. The process according to claim 5 wherein said halogenating agent is hexachloroethane.

11. A writing instrument comprising, as the marking element thereof, a vulcanizate of halogenated polymer prepared according to the process of claim 1 containing from 5 to 75 parts by weight of a pigment selected from the group consisting of carbon black, graphite, titanium dioxide, malachite, and iron oxide.

12. A vulcanizable product prepared according to the process of claim 1.

13. A product of the vulcanization of a halogenated material prepared in accordance with the process of claim 1.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,850,490

September 2, 1958

Peter J. Canterino et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 64, for "350-400^o" read -- 250-400^o --; column 4, line 23, for "ethylene is" read -- ethylene in --; column 7, line 23, in the equation for "1.303" read -- 2.303 --; column 8, line 17, for "halognating" read -- halogenating --.

Signed and sealed this 21st day of April 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

June 20, 1961

Z. LORENIAN

2,988,784

MANUFACTURE OF PENCILS AND OTHER SHAPED ARTICLES

Filed July 26, 1956

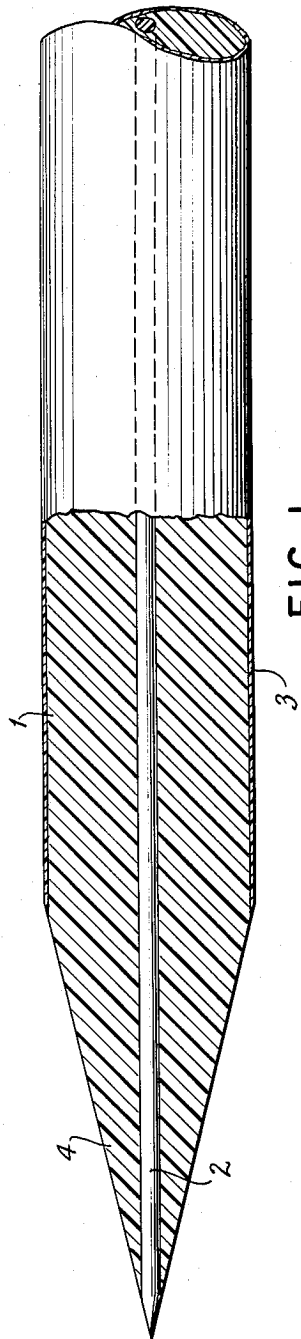


FIG. 1

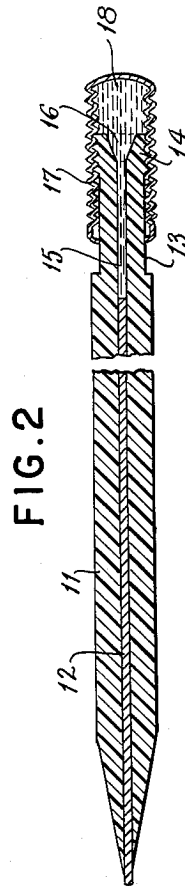


FIG. 2

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MANUFACTURE OF PENCILS AND OTHER SHAPED ARTICLES

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My invention relates to the manufacture of pencils and components thereof, such as pencil sheaths and pencil cores, and other shaped articles from thermoplastic compositions and is herein disclosed as a continuation-in-part of my copending application Serial No. 100,822, filed June 23, 1949, now abandoned.

In one of its more specific aspects, my invention relates to writing pencils of the scissible type, that is pencils which can be sharpened by a knife or pencil sharpener like ordinary wood-sheathed pencils.

For that reason, the invention is hereinafter mainly described with reference to writing, drafting, coloring or copying pencils, although it should be understood that my invention, in its broader aspects, applies generally to shaped articles made by shaping a thermoplastic mixture in dry condition under heat and pressure.

Heretofore the sheaths of pencils have ordinarily been made of wood. The wood must be of special quality since the finished pencil must not only be capable of being easily sharpened but the sheath must also form the support for the relatively fragile core. Moreover, the process of manufacturing pencils with conventional wooden sheaths and lead, including twelve to twenty-four operations, is expensive and time-consuming, and a large quantity of wood is wasted. The wood is first cut into small slabs which are then grooved. The lead is inserted in the groove of one slab, a second grooved slab is placed upon the first one to enclose the lead, and the two grooved slabs are then glued together. Furthermore, in order to obtain satisfactory cutting capacity the grooved wooden slabs in the course of manufacture must undergo special treatment. Pencils are exposed to varying temperatures and varying degrees of humidity. The wooden sheath of the conventional pencil tends to expand or to dry out, causing the lead to loosen in the sheath and to slip out or break in the pencil particularly if the two slabs of the sheath have different fibrillation or grain.

Another disadvantage of the wooden sheath is that the grain of the wood tends to guide the knife when sharpening the pencil so that a person sharpening a pencil manually cannot always control the direction of cutting in the desired manner. Furthermore, when sharpening a conventional pencil, a certain minimum thickness of chip must be cut. As a result the pencil is prematurely used up. When the pencil is sharpened by pencil sharpening apparatus, the sharpened portion of the wood is left rough because the knives or cutting blades of the pencil sharpener operate across the grain. This roughness may be disagreeable when using the pencil.

In the conventional pencil, moreover, the lead or core is a mixture of clay and graphite, the clay serving as a binder. The hardness of the lead is controlled by varying the proportion of clay in the mixture. The clay also influences the shade of the lead. Moreover, the clay, particularly in a hard pencil, scratches the paper; and when the paper is erased the scratches are not removed. If the proportion of clay is reduced, the breaking strength of the lead is reduced too, and the rate of wear of the pencil is increased; and the pencil is prematurely used up.

In copying pencils or colored pencils, clay cannot be used as a binding agent since the dyestuffs would be destroyed by the baking operation required in the case of

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a ceramic lead. Therefore, hydrophilic binders, such as tragacanth are used. These leads or cores are very sensitive to atmospheric influence.

Because of the disadvantages with lead and sheaths as previously made, there have been prior suggestions that artificial, synthetic materials be used for sheaths, or cores, or for both sheaths and cores. Thus, it has been proposed to manufacture pencil sheaths by extrusion and subsequent drying of an aqueous pulp of wood or paper; but all attempts in this direction have been unsuccessful because of the necessity of expelling large amounts of water from the extruded strand and the low quality of the finished pencils in which the lead or other marking core is apt to be loosened in the sheath due to shrinkage and expansion of the moisture-sensitive sheath material.

As will be more fully set forth below, my invention requires the dry shaping, under heat and pressure, of a thermoplastic composition comprising a water-insoluble synthetic thermoplastic resin. Now, such thermoplastic synthetic resins, used as a binder, have generally a relatively small binding capacity as compared with natural resins and thermosetting resins such as phenolic resins. Water-insoluble synthetic thermoplastic resins, therefore, when used in small quantity as a binder for a large quantity of comminuted and voluminous material, such as wood flour or other cellulosic fibres, do not bind such materials in such a manner as to impart to the shaped article the resistance and strength needed for the intended use of the particular article. Besides, comminuted wood, such as wood flour and other fibrous materials, as well as a number of comminuted mineral substances such as kaolin, are sensitive to moisture, and a small proportion of synthetic water-insoluble thermoplastic resin, even if moisture-insensitive as such, does not have the capacity of rendering the composition practically insensitive to moisture.

Furthermore, some of the mixed substances, notably wood flour, rice or straw and other particulate materials of organic origin, tend to decompose or become carbonized or otherwise impaired when subjected to the plasticizing temperature and pressure required for the thermoplastic binder when the mixed composition is being shaped into an article, especially if some delay in the extrusion press or other heated molding equipment is encountered.

It is an object of my invention to produce thermoplastic pencil components such as pencil sheaths and pencil cores, or complete pencils and other shaped articles that, aside from having all desired qualities of the corresponding conventional articles, afford being made at low cost and have the advantage of being practically insensitive to moisture and dryness and preferably also fire retardant, and which possess the resistance and rigidity or flexibility as required for the intended use of the particular article. Relative to pencil sheaths and similar articles, it is a conjoint object to obtain superior and more uniform scissibility, and as to pencil marking cores and similarly composed articles, it is a conjoint object to obtain improved mark-depositing and sliding ability to minimize scratching the paper, thus generally achieving advantages which the conventional pencils do not have and cannot attain because of the properties of their structural material and because of their method of manufacture.

To achieve these objects, and in accordance with my invention, I produce the pencil components or complete pencils and other shaped articles by shaping, in dry condition under heat and pressure, a homogeneously mixed composition of three basic components, namely:

(1) A major quantity of a comminuted main ingredient, such as wood flour and/or the other particulate sub-

stances mentioned below, which determines the character of the finished shaped article;

(2) A minor quantity of waxy substance such as chlorinated naphthalene and/or the other substances mentioned below; and

(3) A minor quantity of a binder consisting essentially of substantially water-insoluble and practically moisture-insensitive thermoplastic synthetic resin such as polyvinyl chloride and/or the other synthetic thermoplastic resins mentioned below.

All quantities and percentages herein referred to are by weight.

I have found that, as a general rule, the desired superior results are obtained only if the quantity of the binder is smaller than that of the particulate main ingredient, and if the quantity of waxy substance is always smaller than that of the binder in order to preserve the desired binding capacity of the binder needed for mechanical resistance and strength and stability of the article. For best results in most cases, particularly for pencils and pencil components such as scissible pencil sheaths and leads or cores, it is preferable to have the quantity of main ingredient larger than the sum of the respective quantities of the two other basic ingredients.

A suitable range of composition, relating to 100 parts by weight of main ingredient, is about 1 to about 70 parts, preferably more than 5 parts, of waxy substance, and about 10 to about 90 parts of the specified binder, the latter quantity being in each case larger than that of the waxy substance. Under such conditions, the character of the finished article is substantially determined by the particulate main ingredient, as contrasted to wax crayons in which waxy and/or fatty substances predominate and occur in a quantity as large as, or larger than, that of the binder.

It will be understood that each of the three basic ingredients may comprise more than one individual substance and that the usual plasticizer, coloring agents or the like auxiliary additions may be present depending upon the intended use or appearance of the article, as will be more fully described below. The composition after being prepared into a homogeneous mixture, is not suitable for aqueous or wet shaping methods but must be shaped in dry condition under heat and pressure whereafter the shaped articles are immediately ready for use. The shaping may be done by extrusion, injection molding, compression molding, pressing or calendaring. I have found that extrusion of the composition by means of a screw press is particularly favorable for making pencils, pencil components, as well as profiled, tubular or flat articles in general.

When mixing the three basic ingredients together, it is necessary to follow a certain sequence or course of mixing operation so that the waxy substance can become fluid or liquid and thus can coat or impregnate the individual particles of the main ingredient before the thermoplastic resin can have a bonding effect upon the waxy substance or the main ingredient. This will be further explained in a later place as the necessity for proper mixing will best be understood from the more detailed description of the basic ingredients and their mutual coaction given presently.

(a) As mentioned, the particulate main ingredient may consist of, or comprise, comminuted wood such as wood flour. This material, preferably used in pencil sheaths, is sensitive to moisture and dryness; and it is one of the outstanding advantages of the invention that such materials, used as herein disclosed, do not impart such detrimental sensitivity to the finished article. Other main ingredients of the same type, i.e. sensitive to moisture and dryness, are various forms of wood dust, wood fibres and such other cellulosic fibre materials as straw meal, rice flour and paper flour, all subject to "working" when exposed to moisture or dryness.

(b) Also suitable as main ingredients for the purpose of the invention are particulate substances that are practically sensitive to moisture but insensitive to dryness,

namely such mineral or organic substances as kaolin, lithopone, clay, barium sulphate, bone flour, cotton, wool, asbestos fibre and similar materials.

(c) Comminuted substances that are virtually insensitive to moisture and dryness are likewise applicable as main ingredients and, as in the case of pencil leads, may have to be used for special purposes. Such substances, for example, are graphite, glass meal, glass fibre or glass wool, metal dust, and the like. Excepting the use of graphite for graphite leads, these insensitive ingredients, in general, are not suitable for scissible pencils; but they can be used as main ingredients for the manufacture of pencil sheaths to be used with sliding leads or cores, that is for sheaths that need not be sharpened, and for other shaped articles not requiring scissibility.

The various substances that form the main ingredient may be used in any desired mixture with one another. It is apparent that the main ingredient must be stable and compatible with the other two basic ingredients, waxy substance and binder, under the conditions obtaining during the shaping operation. The above-specified particulate substances meet this requirement, but I have found that comminuted cork used as a main ingredient produces inferior results because when a mixture of cork particles, waxy substance and thermoplastic binder is heated to a temperature of about 135° C. or more and is mixed or worked under heat and pressure in a closed container, such as in an extruder, the cork particles, despite the waxy coating, commence to decompose and evolve gas which sometimes causes explosions. Besides, comminuted cork, due to its structural constitution, does not impart to the shaped article the strength and resistance obtained, for instance, with wood flour or wood dust. A pencil sheath made with comminuted cork is too yielding to permit satisfactory sharpening by means of a knife or pencil sharpener. For these reasons, the use of comminuted cork is not favorable for the purposes of the invention.

The water-insoluble thermoplastic resin used as a binder is preferably practically insensitive to moisture and may consist essentially of polyvinyl chloride (preferably made by the suspension process), copolymers of vinyl chloride, polyethylene (preferably low-pressure polyethylene), ethyl cellulose, cellulose acetate, cellulose butyrate, polyvinyl butyrate, and other water-insoluble thermoplastic synthetic resins. The preferred choice in each case is determined by the fact that the binder must have a bonding effect upon the two other basic ingredients and must be compatible with the waxy ingredient. Conventional plasticizers, stabilizers and/or lubricants may be added to the binder, as well as small quantities of water-insoluble natural resins and/or thermosetting resins as further described below.

The waxy substance, practically insensitive to moisture, used as the third basic ingredient of the composition, may consist of any water-insoluble waxy substance of mineral, vegetable, animal or synthetic origin such as paraffin, ceresin, bee's wax, osokenite, carnauba wax, Chinese or Japan wax, montan wax, chlorinated naphthalene, chlorinated paraffin or other chlorinated waxy substances, as well as fatty materials similar to wax, for instance, spermacetti. I prefer using waxy substances, such as those mentioned, which are practically insensitive to moisture. An essential criterion for all such substances for the purpose of the invention is the fact that they are water-insoluble and become liquid or fluid when heated in dry condition at a temperature not higher than the softening or molding temperature of the thermoplastic-resin ingredient of the composition, so as to form a coating or impregnation on the particulate main ingredient. The waxy substance must be compatible with the main ingredient and, particularly, also with the binder which is used in a larger quantity than the waxy substance. Some of the waxy substances, such as chlorinated naphthalene, are preferable because of their fire-retarding or fire-proofing quality. For economical reasons,

I further prefer using a waxy substance lower in cost than the thermoplastic binder as is also the case with chlorinated naphthalene, although the more expensive waxy substances are likewise economically applicable in compositions containing a relatively small proportion of such substances in comparison with the larger amount of binder and, above all, with the larger amount of main ingredient.

If the comminuted main ingredients of the composition are sensitive to moisture and dryness as is the case, for instance, with wood flour, then the waxy substances, which are liquid when heated, cover and impregnate the individual particles of the main ingredients; and if the main ingredients are porous the waxy substances penetrate into the pores of the particles of main ingredients thus making them practically inert and insensitive to moisture and dryness. Besides, if the waxy substances are fire-resistant, as is the case with chlorinated naphthalene, the coated or impregnated particles of the main ingredients are made fire retarding or practically fire-proof.

Furthermore, since the waxy substances are compatible with the thermoplastic synthetic binders, they also have the effect of increasing and/or extending the over-all binding capacity; that is, the quantity of the binder which generally is not liquid when heated to the molding temperature can be kept smaller than otherwise required. In other words, the waxy substances act as an auxiliary to the binder so that a comparatively large volume of main ingredients can be satisfactorily bonded by means of a smaller quantity of binder. In addition, the presence of the waxy substances in the composition imparts to the finished particles a smoother and more agreeable surface, and, as the case may be, it also improves the scissibility of the product.

The waxy substance also acts as a lubricant when the articles are being shaped under heat and pressure so that the usual addition of supplemental lubricant to the mixture can be reduced or omitted.

When making pencil sheaths from the composition, the waxy substances greatly contribute to improved scissibility. When the composition is used for making graphite lead and colored cores for pencils, the waxy substance improves the mark-depositing and gliding ability as well as the scissibility of such leads or cores. As a result, scratching of the paper by the tip of the marking core is greatly minimized or eliminated, even with relatively hard grades of the marking core. These advantages and qualities due to the presence in the mixed composition of water-insoluble and compatible waxy substance is important even if the main ingredient is not sensitive to moisture or dryness as is the case where the main ingredient consists of graphite and article made of the composition consists of a graphite lead for pencils.

As briefly mentioned above, it is an essential requirement for achieving the desired result of the invention that the three basic ingredients be mixed in a manner that permits the waxy substance to become liquefied under heat and to become incorporated or impregnated into the particular main ingredient before the thermoplastic synthetic binder can become effective to bond either the main ingredient or the waxy substance. This requirement will be understood if one considers that the waxy substance becomes liquefied more readily and at lower temperature than the thermoplastic synthetic resin and requires only heat but no pressure to thus change its consistency. In contrast, the water-insoluble thermoplastic synthetic resin not only requires a higher temperature as well as pressure but it also does not become as fluid as a dry waxy substance. Consequently, when the preparation of the composition is so conducted that the waxy substance can liquefy without being bonded by, or incorporated in, the thermoplastic binder, then the good dispersion ability of the wax takes care of having the particles of the main ingredient covered or preferably impregnated by the liquid wax, before the binder, becom-

ing plastic or viscous under heat and pressure, can bond the coated particles together.

There are several ways of properly preparing the mixed composition. The first and preferable way is to first mix the waxy substance in dry condition, that is without solvent, with the particulate main ingredient while the waxy substance is heated and liquefied. In this manner, the particles of the main ingredient are first covered or impregnated with the waxy substance. The next step is to mix the wax-coated or impregnated main ingredient with the binder.

A second, generally less satisfactory or less reliable way, is to mix the comminuted main ingredient at once with the waxy substance and with the binder. In this case, when heat and pressure are applied, the waxy substance will liquefy more rapidly and at a temperature below the plasticizing point of the binder so that the liquefied waxy substance can cover, or enter into, the main ingredient before the binder becomes plastic under heat and pressure to provide the necessary bonding between the coated particulate main ingredients.

In contrast, I have found that no satisfactory results are obtained under otherwise the same conditions if the waxy substance is first mixed with the binder and thereafter the mixture of waxy substance and binder is mixed together with the main ingredient. I believe the reason for the failure of producing the desired result in the last-mentioned manner is the fact that when the waxy substances are first combined with, or incorporated into, the thermoplastic binder, the waxy substances are no longer readily liquefied at low temperature but become plastic together with the binder, so that they do no longer have the above-mentioned dispersion capacity and are prevented from covering or impregnating the comminuted, voluminous main ingredient. As a result, much larger proportionate quantities of binder are necessary, and the article shaped from the mixed composition, aside from being generally more expensive, do not have the same physical characteristics as those produced with the above-mentioned proper methods of preparation.

It will be recognized from the foregoing that three general conditions are essential for the invention:

In the first place, the composition must comprise the above-described three basic ingredients, namely a comminuted or particulate main ingredient, a water-insoluble waxy substance, and a water-insoluble thermoplastic synthetic resin, the quantity of waxy substance being smaller than that of the resin; secondly, the three basic ingredients must be mixed together in such a manner that the waxy substance can liquefy and cover or impregnate the main ingredient before the bonding effect of the thermoplastic resin takes effect; and, ultimately, the composition must be shaped under heat and pressure in dry condition, as it is not applicable for use in a wet method such as the above-mentioned processes involving aqueous suspension or pulp masses.

The particular physical properties of the articles made according to the invention depend upon various factors to be chosen in accordance with the particular purpose for which the articles are to be used. One of these factors, for instance, is the proportion of the waxy substance relative to the proportion of the binder as compared with the amount of the comminuted main substance. Another factor is the quantity of the conventional plasticizers which are added to the water-insoluble thermoplastic resin and which generally determines the degree of rigidity or flexibility of the shaped articles. It will of course also be understood that any desired coloring agents may be added to the main ingredients, the waxy substance and/or the binder. The conventional lubricants and stabilizers, if desired, are also applicable.

While, as described above, the quantity of comminuted main ingredients according to the invention, in principle, is larger than the quantity of each of the two other basic ingredients or larger than the sum of both other basic in-

redients, I have found that there exists an exception to this general principle in those cases where the main ingredient consists of comminuted wood or other cellulosic materials that are sensitive to moisture and dryness. In such cases, results satisfactory for some purposes can also be obtained if the quantity of the water-insoluble thermoplastic synthetic resin is made somewhat larger than the quantity of the main ingredient, provided the quantity of the waxy substance remains smaller than the individual quantities of main ingredient and thermoplastic binder. Such compositions, comprising a thermoplastic binder in a quantity of up to about 20% larger than the quantity of the main ingredient, afford the production of shaped articles of great mechanical resistance and strength and improves insensitivity to dryness and moisture. On the other hand, such increase in quantity of binder relative to the main ingredient has the disadvantage that the cost of the shaped article made of such a composition is higher and that the scissibility of the shaped articles, particularly those of pencil sheaths, is impaired or, if the composition is used for pencil leads or marking cores, the marking ability is likewise impaired.

The invention will be more fully understood from the examples described in the following. It should be understood that the examples are not presented in a limited sense but that various modifications are applicable in accordance with the foregoing explanations and within the scope of the claims annexed hereto. All proportions and percentages given in the examples are by weight.

Example 1

The following composition is suitable for the manufacture of scissible pencil sheaths and other shaped articles that are woodlike in general character and/or appearance:

- 100 parts wood flour (main ingredient)
- About 20-40 parts chlorinated naphthalene (waxy substance)
- About 30-55 parts polyvinyl chloride, preferably made by the suspension process (binder)
- 3-20%, relative to the amount of binder, of dibutyl phthalate (plasticizer)
- 1-3%, relative to the amount of binder, of lead stearate (stabilizer)
- 1-5 parts of cedar brown mixed with orange dyestuff and mixed with 5-10 parts titanium white (coloring substance)

It will be understood that the specific composition to be chosen from the indicated ranges depends upon the desired degree of scissibility, rigidity or other physical properties which the shaped article is supposed to possess. For instance, I have found the following specific compositions to be particularly useful for scissible wood sheath of pencils and other woodlike articles of similar appearance and rigidity:

- 100 parts wood flour (main ingredient)
- 30 parts chlorinated naphthalene (waxy substance)
- 45 parts polyvinyl chloride (binder)
- 10%, relative to the amount of P.V.C., of dibutyl phthalate (plasticizer)
- 2%, relative to the amount of binder, of lead stearate (stabilizer), 4% relative to the total composition, of zinc stearate (lubricant)
- 2 parts of cedar brown and 1 part of orange dyestuff mixed with 5 parts of titanium white to serve as a coloring substance

Regardless of the specific composition chosen for the particular shaped article to be produced, I prefer preparing the above-described combination of ingredients in the following manner:

The wood flour is to be used in dry condition. For this purpose the wood flour is placed into a mixer and heated under vacuum to a temperature of about 130°

C. to 140° C. The mixer is maintained under vacuum so that the moisture of the main ingredient is withdrawn. Then, a mixture of the waxy substance with the above-mentioned coloring substances is sprayed dry, in heated and melted form, onto the particles of the main ingredient while the main ingredient is still contained in the mixer and kept under vacuum. The mixing is continued until the mass is substantially homogeneous. The thermoplastic binder is mixed with the plasticizer and stabilizer and, as the case may be, also with the lubricant, to form a separate batch. Then the mixture of binder and auxiliary additions is added to the impregnated main ingredient. This is also done in the mixer and preferably while the mixer is kept under heat and vacuum. The vacuum in the mixer during the above-described operations may be kept, for instance, at 5-10 m. Hg, and the temperature maintained during the mixing operation and while the binder is being added may be kept, for example, between about 130° and 160° C. After the mixture is made homogeneous, it is discharged from the mixer and thereafter calendered under heat and pressure, for instance at a temperature of 120° to 150° C. Thereafter the calendered composition is milled and is subjected in dry condition to shaping under heat and pressure. The preferred shaping operation for the manufacture of pencil sheaths and various other shaped articles is by means of an extrusion screw press and at a temperature preferably between about 120° and about 160° C. It is also possible to shape the composition as it comes out of the mixer without calendering, but I prefer adding the calendering step because it results in a better compacted and homogenized material. The shaped articles thus produced are woodlike in appearance and general character and are readily scissible, the main ingredient, namely the wood flour, determining the overall character of the product.

Another method is to dry the wood by any other method than vacuum in this case. Then the wood flour may simply be impregnated in hot condition with the liquefied waxy substance without the use of a vacuum, and the binder may thereafter be added likewise without the use of a vacuum. However, for best results and best uniformity of the products, I prefer preparing the composition under vacuum as described above. As mentioned, there is also the possibility of mixing the main ingredient with the waxy substance and at the same time with the binder, but I consider the latter method less preferable to those described in the foregoing. In any case, the waxy substance must not be permitted to become combined with, or incorporated into, the thermoplastic binder before the waxy substance is joined with the main ingredient.

Example 2

The following composition is suitable for the manufacture of scissible colored cores for pencils and other shaped articles of distinctive color:

- 100 parts kaolin
- 15-45 parts chlorinated naphthalene (waxy substance) to which are added 2-15 parts Sudan red (main ingredient)
- 30-50 parts polyvinyl chloride (binder)
- 3-15%, relative to the amount of P.V.C., of tricresyl phosphate (plasticizer)
- 1-3%, relative to the amount of binder, of lead stearate (stabilizer)
- 2-8 parts of calcium stearate (lubricant)

This composition is prepared and fabricated in accordance with one of the methods described above with reference to Example 1.

The particular proportion of substances to be chosen within the ranges above indicated, as well as the particular coloring substance added to the main ingredient, depend upon the desired physical characteristics and color of the colored marking core or other shaped article to

be produced. For instance, in order to produce a marking core in blue color, the following specific composition was found satisfactory:

- 100 parts kaolin to which are added 5 parts Prussian blue and 10 parts titanium white (main ingredient)
- 40 parts chlorinated naphthalene (waxy substance)
- 45 parts of polyvinylchloride, made by suspension process (binder)
- 12% of dioctyl phthalate, relative to the weight of the polyvinylchloride (plasticizer)
- 1.5% lead stearate (stabilizer), relative to the weight of the polyvinylchloride
- 3 parts of calcium stearate (lubricant)

Example 3

The following composition is suitable for the manufacture of graphite leads for pencils and other shaped articles in which graphite is the main ingredient and determines the character and appearance of the finished article:

- 100 parts graphite powder, preferably mixed in equal proportions of crystalline graphite and amorphous graphite
- 2-15 parts lamp black, which forms part of the main ingredient but also contains waxy substances
- 20-35 parts chlorinated naphthalene (waxy substance)
- 25-45 parts polyvinylchloride (binder)
- 2-15% dioctyl phthalate (plasticizer), relative to the weight of the binder
- 1-3% lead stearate (stabilizer) relative to the weight of the binder
- 2-10 parts of zinc stearate (lubricant)

As in the previous examples the specific composition best to be chosen from the indicated ranges depends upon the desired specific character, for instance hardness, of the product. One of the specific compositions which I have found preferable is the following:

- 50 parts amorphous graphite
- 50 parts crystalline graphite
- 5 parts lamp black
- 30 parts chlorinated naphthalene
- 40 parts polyvinylchloride (suspension process)
- 10% tricresyl phosphate (plasticizer), relative to the weight of the P.V.C.
- 2% lead stearate (stabilizer), relative to the weight of the binder
- 4 parts zinc stearate (lubricant)

The composition according to this example may be prepared and fabricated in accordance with the methods described with reference to Example 1. However, since graphite is not water-sensitive, it is not necessary to work under vacuum, and the other methods referred to under Example 1 are less objectionable. However, I prefer spraying and dispersing the waxy substance onto the graphite particles under vacuum to obtain a more uniform coating of the particles.

It will be noted that in all foregoing examples the waxy substance consists of chlorinated naphthalene and the binder consists of polyvinylchloride. The use of the same waxy ingredient and the same binder ingredient in these examples serves the following purpose. While articles according to the respective examples, such as pencil sheaths and pencil cores, can be manufactured individually and separately from one another, it is advantageous in the manufacture of pencils to extrude the sheath material onto and around a marking core material which is being extruded simultaneously within the same extrusion device, so that the pencil core and the sheath are manufactured and combined with each other within one single operation. As a result, the shaped sheath composition and the shaped core composition emerge at the same rate from a single nozzle at the end of the extrusion ma-

chine, preferably an extrusion screw press. While details of this manufacturing method are not essential to the present invention proper, reference may be had, if desired, to the methods and extrusion devices illustrated and described in my copending applications Serial No. 100,823, filed June 23, 1949, now Patent No. 2,769,201, and Serial No. 279,496, filed March 31, 1952, now Patent No. 2,790,202. When using for such simultaneous extrusion of pencil sheaths and pencil cores such compositions as exemplified by Example 1 on the one hand, and Example 2 or 3 on the other hand, the similarity of the thermoplastic binders and waxy substances in the sheath and core compositions has the result that the extruded core becomes tightly bonded or welded together with the pencil sheath so that the core in the finished pencil will never become loose from the sheath and will not break in the pencil when the pencil is dropped onto a hard floor or otherwise subjected to impact. When such a pencil is sharpened by a knife or pencil sharpener, each individual chip shows that the graphite or other core material is coalesced with the sheath material into one integral body. It should be understood, however, that other waxy substances or other binders that are mutually compatible may readily be used instead of those given in the foregoing examples. Thus, paraffin may serve as a waxy substance with a binder consisting of ethyl cellulose with which it is compatible. In other words, the particular binder and the particular waxy substance should be chosen from the viewpoint of compatibility relative to each other.

Example 4

The following composition is suitable for manufacturing pencil sheaths and other shaped articles:

- 250 parts wood flour
- 5-25 parts chlorinated naphthalene
- 0.1-3 parts coloring substances

These materials are intimately mixed together in hot condition. Then the following materials are intimately admixed also at elevated temperature:

- 100 parts polyvinylchloride and an admixture of 2 to 40 parts phenol formaldehyde resin
- 2-10 parts orthonitrodiphenyl
- 1-5 parts tricresylphosphate
- 2-8 parts calciumpalmitate (lubricant)
- 5-10 parts zinc oxide
- 0.1-2 parts coloring substances

This dry blend is formed at 110-130° C. under pressure in accordance with one of the methods mentioned in Example 1.

Example 5

Another composition for manufacturing pencil sheaths and other shaped articles consists of:

- 300 parts wood flour
- 5-30 parts water-insoluble waxes with an addition of 2 to 10 parts of water insoluble fats

This group of materials is intimately mixed together. To the mixed group are added the following materials:

- 100 parts ethylcellulose or celluloseacetatebutyrate (binding agent)
- 2-8 parts zinc stearate (lubricant)
- 0.5-3 parts coloring substances

These materials are mixed together. To the binding agent may be added as additional binder:

- 2-40 parts of thermosetting synthetic resins, and/or
- 2-40 parts of thermoplastic natural resins

To this blend may be added 2-10 weight parts of ammonium bicarbonate or similar gas-producing agent. The dry blend is formed at 120-140° C. under pressure. The mixing and shaping can be done as in the Example 1.

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Example 6

For manufacturing of graphite-leads for pencils and other shaped articles, the following materials in proportions as follows are intimately mixed together:

- 100 parts graphite (main ingredient)
- 1-15 parts carbon black (which form part of the main ingredient but also contains waxy substances)
- 5-20 parts water-insoluble waxes with an addition of 2 to 10 parts water-insoluble fats

After these materials are mixed together, the following materials are added:

- 20-50 parts polyvinylchloride or copolymer of vinylchloride (binding agent)
- 0-10 parts orthonitrodiphenyl
- 1-30 parts cadmium ricinoleate (lubricant)

All these materials are mixed together. To the binding agent may be added as additional binder:

- 2-40 parts of thermosetting synthetic resins, and/or
- 2-40 parts of thermoplastic natural resins

This dry blend is formed at 120-160° C. under pressure as described with reference to Example 1.

Example 7

For manufacturing colored leads for pencils and other shaped articles the following materials are intimately mixed together in hot condition:

- 100 parts clay or similar materials
- 5-50 parts coloring substances
- 2-10 parts water-insoluble fats
- 5-20 parts waxes

After these materials are mixed together, the following materials are added:

- 20-35 parts ethylcellulose or cellulose acetatebutyrate (binding agent)
- 0-15 parts paratoluol sulphonamide or triphenylphosphate
- 5-30 parts barium ricinoleate (lubricant)
- 1-3 parts coloring substances

All these materials are mixed together. To the binding agent may be added as additional binder:

- 2-40 parts of thermosetting synthetic resins, and/or
- 2-40 parts of thermoplastic natural resins

This dry blend is formed at 100-120° C. under pressure as described in Example 1.

Example 8

The following composition is suitable for pencil sheaths and other shaped articles of woody character that have a lesser degree of scissibility than the product resulting from Example No. 1:

- 100 parts cellulose acetate (of the kind suitable for injection molding or extrusion) are dissolved in 400 parts acetone

This solution is kneaded together with:

- 100 parts wood dust
- 50 parts straw meal
- 50 parts rice flour
- 40 parts dibutyl phthalate
- 10 parts paraffine
- 3 parts zinc stearate
- 1 part titanium white

After or while preparing a homogeneous mixture of all ingredients, the solvent is evaporated by heating, preferably in vacuum, so that a completely dry mass is obtained. This dry mass is shaped, preferably by extrusion in a screw press, in dry condition under heat and pressure as described earlier in this specification.

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Example 9

Composition for colored leads and other colored shaped articles:

- 5 100 parts barium sulphate and 3-20 parts chrome yellow (main ingredient)
- 15-45 parts carnauba wax
- 30-50 parts ethylcellulose (binder)
- 3-15 parts ricinoleate (plasticizer)
- 10 The composition is prepared and shaped, preferably extruded, as in Example 1.

Example 10

Composition for copying or indelible marking cores:

- 15 70 parts kaolin and 30 parts talcum (main ingredient)
- 5-20 parts methyl violet
- 20-60 parts chlorinated naphthalene
- 40-90 parts low-pressure polyethylene
- 20 The mixture is prepared and shaped as described with reference to Example 1.

Example 11

- 25 As mentioned, the rigidity or flexibility of the shaped article depends upon the proportion of the conventional plasticizer added to the water-insoluble thermoplastic synthetic resins that form the binder of the combination of ingredients. Accordingly, the following example relates to a composition for the production of comparatively rigid articles, such as the sheaths of slidable-core pencils, which need not be sharpened and need not be scissible:
- 30 40 parts paper flour
- 30 parts cotton flour
- 30 parts comminuted glass fibres
- 35 2-10 parts Prussian-blue coloring substance (all forming together the main ingredient)
- 10-30 parts ceresin (waxy substance)
- 40-60 ethylcellulose (binder)
- 40 0-20 tricresyl phosphate (plasticizer)

The above ingredients are to be prepared as in Example 1.

Example 12

- 45 This example also relates to the manufacture of pencil sheaths and other shaped articles which, like the sheaths of slidable-core pencils, need not be scissible:

- 70 parts wood dust
- 30 parts comminuted asbestos fibers
- 50 2-10 parts vermilion chrome red (all forming together the main ingredient)
- 30-60 parts of a mixture of chlorinated naphthalene with 2-10 parts polyethylene (waxy substances)
- 60-90 parts polyvinylchloride preferably made by the suspension process (binder)
- 55 10-25% dibutyl phthalate (plasticizer), in proportion to the amount of binder
- 0.5-3% lead stearate (stabilizer), in proportion to amount of binder

The above ingredients are to be prepared as described for Example 1.

Example 13

- 65 This composition is given as exception to the above-mentioned general rule of proportioning of main ingredient and binder, and is suitable for making sheaths for slidable-core pencils or other shaped articles, preferably by extrusion in a screw press:

- 80 parts wood flour
- 20 parts cotton flour, and
- 2-10 parts coloring substances (all forming together the main ingredient)
- 20-30 parts montan wax
- 5-10 parts paraffin, and
- 75 10-15 chlorinated naphthalene (waxy substances)

70-80 parts ethylcellulose, and
30-40 parts cellulose butyrate (binders)

To the binder is added: 2-20 parts dibutyl phthalate (plasticizer).

This combination of ingredients is prepared and shaped as described for Example 1.

It will be recognized that in Example 13, each of the three basic ingredients is composed of more than one component and that, while the quantity of the waxy substances is smaller than the respective quantities of main ingredient and binder, the total quantity of binder is somewhat larger than the total quantity of the main ingredients. However, the total quantity of the main ingredient is still large enough in comparison to the binder quantity to determine the character of the shaped article. The articles made of such a combination of ingredients have greater mechanical resistance and strength than those made according to the other examples but, as explained, some disadvantages must be put up with.

Example 14

The following composition is suitable for pencils, and particularly other shaped articles, of greater flexibility than obtained with the compositions according to the preceding examples:

100 parts wood flour to which are added 2 parts of cedar brown, 2 parts of orange pigment and 4 to 20% titanium white, all forming part of the main ingredient and imparting a woody color to the product

35 parts chlorinated naphthalene (waxy substance)

60 parts polyvinylchloride, made by the suspension process (binder)

35% tricresyl phosphate (plasticizer) in proportion to the weight of the binder

2% lead stearate (stabilizer) in proportion to the weight of the binder

3% aluminum stearate (lubricant) in proportion to the weight of the total composition

This composition is prepared and fabricated as described in the foregoing, particularly with reference to Example 1.

As is apparent from the examples, the water-insoluble thermoplastic synthetic resins used as binder may be admixed with conventional and compatible, preferably non-volatile plasticizers in order to impart to the finished product the desired degree of rigidity or flexibility. The amount of added plasticizer may range up to about 100% of the thermoplastic binder. The conventional stabilizers and/or lubricants may also be added, as is apparent from the examples. The amount of such additions of stabilizers may be up to about 5% of the binder and the amount of the lubricant may be up to about 10% to the amount of the whole composition. It will further be recognized from Examples 4, 5, 6 and 7 that the water-insoluble, plastic synthetic resins may be admixed with small quantities of compatible water-insoluble and preferably moisture-insensitive thermosetting resins such as phenol formaldehyde or urea resins, or those available under the trade name Desodor or Desmophen and other similar thermosetting resins and/or water-insoluble and preferably moisture-insensitive natural resins such as colophony, copal resins, damar resins, kauri resins, and other similar natural resins. Such additional thermosetting and natural resins have binding effect in addition to that of the main binder which is always formed by the water-insoluble thermoplastic synthetic resins. The proportion of such additional thermosetting and natural resins may amount up to 40% of the total weight of the water-insoluble thermoplastic synthetic resin. It will be understood that such additional small quantities of natural or thermosetting resin may also be added to the binders of the other examples presented in the foregoing.

If porosity of the pencil components or other shaped articles is desired, a small quantity of gas-producing agent such as ammonium bicarbonate, calcium carbonate or similar substances, as exemplified by Example 5, may be added to the composition. Such gas-producing agents have the effect of reducing the density and weight of the articles by the resulting pores; they also impart better scissibility to pencil sheaths, pencil leads or other marking cores, and also improve the mark-producing ability of such marking cores. The proportion of the gas-producing agents may vary from 2 to 20% of the total amount of components. The gas-producing agent is mixed with the other ingredients and becomes effective to evolve gas and to form a porous structure when the articles are being shaped in dry condition under heat and pressure. The gas-producing agent may be added to any of the compositions according to the above-presented examples.

As mentioned above, there are essentially the following ways of preparing the mixed compositions to be used according to the invention.

The first way, particularly important when the main ingredient is sensitive to moisture, is to first place the main ingredient under vacuum in a heated mixer so that practically all moisture is exhausted under heat and vacuum. Thereafter the dry waxy substance, in hot and liquid condition, is sprayed onto the particles of the main ingredient during continued mixing operation and during continued maintenance of vacuum so that the particles become impregnated or coated with the waxy substance. Thereafter, preferably always under vacuum and heat, the binder and any further components are introduced into the mixer; and after all components are mixed together to a homogeneous composition, the articles to be produced are shaped in dry condition under heat and pressure, preferably by extrusion with the aid of a screw press.

The second way of preparing the compositions is to calender, or mix under heat and pressure, the main ingredient with the waxy substances, whereby the moisture of the main ingredient is evaporated and the particles of main ingredient are covered or impregnated with the waxy substance. When this condition is reached, the binder and any supplementary materials are added while the calendaring or mixing is continued under pressure until a homogeneous composition is obtained. This composition is then shaped in the dry state under heat and pressure, preferably by extrusion.

The third way is to mix all ingredients together under heat and thereafter apply pressure and to then shape the article from the homogeneous mixture in the same manner as mentioned above.

I have found that in most cases the first way of preparation affords superior results in comparison with the second way, but that the second way of preparation is applicable with main substances that are not sensitive to moisture as in the case with graphite. The third way is the least preferable of the three methods and may have inferior results with moisture-sensitive main ingredients.

It will be understood that the physical characteristics of the shaped articles made according to the invention are, to some extent, also dependent upon the pressure applied to the composition during the shaping operation, preferably by extruding the material under heat and pressure in an extrusion screw press. This pressure is determined by the dimensions and length of the extrusion nozzle as well as by the normal operating pressure and temperature of the nozzle. The pressure conditions, in general, can be modified to some extent in accordance with the desired density of the product.

Embodiments of pencils which can be made in accordance with the present invention are illustrated by way of example in the accompanying drawing showing in FIG. 1 a partial and partly sectional view of a scissible

pencil, and in FIG. 2 a longitudinal section of a slidable-core pencil.

The pencil according to FIG. 1 comprises an extruded thermoplastic sheath 1 made, for instance, in accordance with Example 1, and a likewise extruded lead or marking core coalesced with the sheath material and made by extrusion of a thermoplastic material, for instance, according to Example 2 or 3. The sheath has a coating 3 of thermoplastic varnish which may be extruded onto the surface of the sheath simultaneously with the extrusion of sheath and core. An extrusion apparatus suitable for simultaneous production of pencil core, pencil sheath and coating is described in my copending application Serial No. 279,496, filed March 31, 1952, now Patent No. 2,790,202. The coating 3 may be made from a composition obtained by mixing 100 parts polyvinyl chloride, 40 parts tricresyl phosphate, 20 parts ochre, and 10 parts titanium white. As mentioned, the yellow mass thus obtained is spread on the surface of the sheath in the same operation in which the sheath and core are produced. The pencil is scissible, i.e. can be sharpened, as shown at 4, by means of a knife or pencil sharpener.

The pencil shown in FIG. 2 is generally of the mechanical type. It comprises a rigid non-scissible sheath 11 of plastic material made, for instance, according to Example 12. A lead 12 of the ceramic type, consisting of the usual mixture of graphite and clay, is enclosed within the sheath that the lead is immovable radially and can be displaced longitudinally only by application of axial pressure. One end 13 of the sheath is machined to a somewhat smaller diameter and is provided with a screw thread 14. The core channel 15 of the sheath is preferably widened at 16 to provide together with the interior of an interiorly threaded sleeve 17 a sufficiently large space 58 for the reception of a hydraulic medium. The sleeve 17 is in tight threaded engagement with the end portion 14 of the sheath. The hydraulic medium fills the space 18 as well as the adjacent conical bore 16 of the channel 15. By turning the sleeve 17, the core 12 can be made to protrude more or less out of the conical portion of the sheath 11 and, if desired, may also be retracted into the sheath by turning the sleeve in the opposite direction and pressing the core back into the channel.

Various pencils of the type shown in FIG. 2, as well as methods and apparatus for manufacturing them, are disclosed in the copending application for Manufacture of Slidable-Core Pencils, Serial No. 595,454, filed July 2, 1956, now Patent No. 2,902,754, to which reference may be had if desired.

It will be apparent to those skilled in the art, upon a study of this disclosure, that my invention permits a large variety of modifications and hence may be embodied in a manner different from the particular embodiments described herein, without departing from the essential features of my invention and within the scope of the claims annexed hereto.

I claim:

1. A shaped article formed of a mixture comprising a major quantity of a comminuted main ingredient consisting predominantly of wood flour, a minor quantity of chlorinated naphthalene waxy material and a minor quantity of polyvinyl chloride as binder, the quantity of chlorinated naphthalene being less than that of the polyvinyl chloride, the quantity of the main ingredient being greater than the sum of the quantities of chlorinated naphthalene and polyvinyl chloride.

2. A method of making a shaped article, comprising spraying a minor quantity of water-insoluble, water insensitive waxy material in dry liquid condition and under vacuum onto a major quantity of a dry comminuted main ingredient consisting predominantly of cellulose, heating to disperse the waxy material into the comminuted ingredient, admixing a minor quantity of a water-insoluble, water-insensitive thermoplastic resin binder to form a

homogeneous mixture, the quantity of comminuted main ingredient being greater than the sum of the quantities of waxy material being less than that of the thermoplastic resin, the resin being one that is compatible with the waxy material, and shaping said mixture in dry condition under heat and pressure to produce the article.

3. A method of making a pencil sheath, comprising mixing a major quantity of a comminuted main ingredient consisting predominantly of cellulose, a minor quantity of water-insoluble, water-insensitive waxy material, heating to melt the waxy material to disperse it into the comminuted ingredient, admixing a minor quantity of a water-insoluble, water-insensitive thermoplastic resin to form a homogeneous mixture, the quantity of comminuted main ingredient being greater than the sum of the quantities of waxy material and thermoplastic resin, the quantity of waxy material being less than that of the thermoplastic resin, the resin being one that is compatible with the waxy material, and shaping said mixture in the substantial absence of moisture in the mixture and under heat and pressure to produce the pencil sheath.

4. A pencil sheath formed of a mixture comprising a major quantity of a comminuted main ingredient consisting predominantly of cellulose, a minor quantity of water-insoluble, water-insensitive waxy material and a minor quantity of water-insoluble, water-insensitive thermoplastic synthetic resin as binder, the quantity of waxy material being less than that of the thermoplastic resin, the quantity of the main ingredient being greater than the sum of the quantities of waxy material and the thermoplastic resin, the resin being one that is compatible with the waxy material.

5. The method defined in claim 3, employed for forming the pencil sheath about a marking core to make a pencil, the method further comprising mixing a homogeneous dry composition of a major quantity of a main core ingredient, a minor quantity of water-insoluble waxy substance and a minor quantity of binder, the main core ingredient consisting essentially of a comminuted marking material which determines the character of the finished article, the binder consisting essentially of water-insoluble, water-insensitive thermoplastic synthetic resin, the resin being one that is compatible with the waxy substance, the quantity of waxy substance being less than that of the binder; and extruding said composition in dry condition under pressure and heat to produce the core, the forming of the sheath also being by extrusion, the mixture forming the sheath being extruded onto and around said marking core as the latter is being extruded.

6. A method of making a pencil marking core comprising mixing a homogeneous dry composition of a major quantity of a main core ingredient, a minor quantity of water-insoluble waxy substance and a minor quantity of binder, the main core ingredient consisting essentially of a comminuted marking material which determines the character of the finished article, the binder consisting essentially of water-insoluble, water-insensitive thermoplastic synthetic resin, the resin being one that is compatible with the waxy substance, the quantity of waxy substance being less than that of the binder; and extruding said composition in dry condition under pressure and heat to produce the core.

7. A method of making a shaped article, comprising mixing a minor quantity of water-insoluble, water-insensitive waxy material in dry condition with a major quantity of a dry comminuted main ingredient consisting predominantly of cellulose, heating to disperse the waxy material into the comminuted ingredient, admixing a minor quantity of a water-insoluble, water-insensitive thermoplastic resin binder to form a homogeneous mixture, the quantity of comminuted main ingredient being greater than the sum of the quantities of waxy material and thermoplastic resin, the quantity of waxy material being less than that of the thermoplastic resin, the resin being

one that is compatible with the waxy material, and shaping said mixture in dry condition under heat and pressure to produce the article.

8. The method defined in claim 7, said cellulose ingredient being wood flour.

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3,262,904

PENCIL LEADS

Filed Aug. 30, 1961

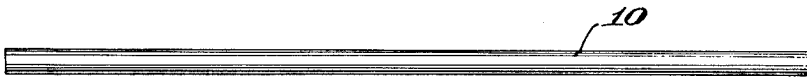


Fig. 1

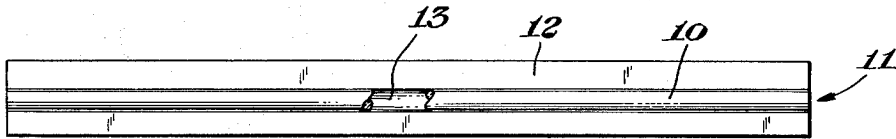


Fig. 2

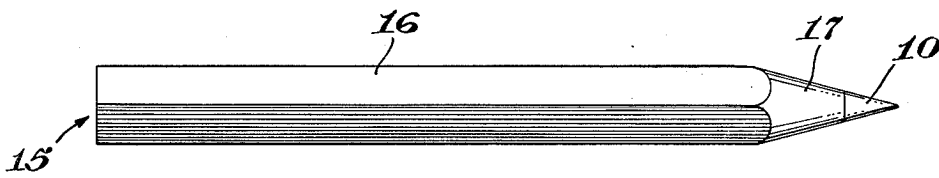


Fig. 3

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3,262,904

PENCIL LEADS

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7 Claims. (Cl. 260-41)

The present invention relates to an improved composition for and a method of manufacturing writing cores. More specifically, it relates to plastic bonded graphite writing core compositions and a method of their manufacture for use as pencil leads.

Commercial pencil lead is composed of four principal ingredients: graphite, clay, gums and waxes. In a typical method of preparing leads according to the art, powdered graphite is combined with purified, wet clay and mixed for several days in ball mills or revolving drums. Water is removed and the mixture is compressed under hydraulic pressure through an extrusion die having orifices the size of the desired leads. The extruded lead is cut into lengths of about seven inches and dried at elevated temperatures for several days. The leads are then baked at approximately 1600° F. for several hours. Losses due to warpage and breakage plus extensive handling requirements add to the cost of the time consuming procedures.

It is an object of the present invention to provide an improved composition and method of manufacture for writing cores which would obviate the costly procedural and handling problems involved in present day pencil lead production while yielding a commercially advantageous writing lead. Other objects of the present invention will become apparent from the following specifications and claims.

It has now been discovered that the qualities of present commercial writing leads are readily reproduced, and in many instances superior properties provided, by an improved composition, which comprises graphite bonded with organic thermoplastic resinous materials. This improved composition possesses properties which enables an improved method of manufacture to be utilized resulting in greatly increased production economy.

For the purpose of facilitating an understanding of the invention, there are shown in the drawings certain forms which are to be understood as not limiting the invention to the precise arrangements and instrumentalities illustrated.

FIGURE 1 is a representation of a writing core 10 in accordance with the invention.

FIGURE 2 is a longitudinal cross sectional view of a pencil 11 comprising a wood case 12 containing a generally centrally disposed groove 13 having a writing core 10.

FIGURE 3 is a side elevation of a pencil 15 comprising a casing 16 with a tapered end 17 and a pointed end writing core 10.

The improved composition consists of amorphous, natural flake graphite which is finely dispersed in organic thermoplastic resins selected to provide a writing lead with the desired strength and writing qualities. Leads containing less than 20 percent thermoplastic resin become objectionably weak while those containing more than 45 percent thermoplastic resin tend to become overly waxy. Maximum strength, however, is not obtained with the 45 percent thermoplastic composition. The flexural strength increases as this percentage is decreased from 45 percent until a point of maximum strength is reached at a composition of approximately 30 percent thermoplastic resins and 70 percent graphite.

In a preferred embodiment, the thermoplastic resinous material comprises two components utilized in a

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ratio which is varied according to the physical properties desired in the writing core. One of the components employed is a rigid thermoplastic resin such as styrene polymer or a copolymer of styrene and acrylonitrile having a flexural strength over 10,000 p.s.i. The other component is a softer, low melt viscosity resin such as branched, high pressure polyethylene.

The improved compositions for writing cores are suitable for use in a continuous extrusion process utilizing conventional plastic processing techniques. The lead produced in this manner is ready for immediate use; a valuable property which makes possible continuous process methods of manufacture. In this improved method of writing core production the appropriate amounts of thermoplastic resins and graphite are intimately blended in conventional plastic processing techniques such as dry blending and mill mixing, extrusion mixing and graphite dispersion in a resin solution followed by evaporation of the volatile component of the dispersion. The mixture is then fabricated into desired shapes by extrusion, molding or similar means.

Flexural strengths of compositions in accordance with the invention were determined by placing writing core samples on supports spaced two inches apart and deflecting the midpoints of these spans at a rate of one-half inch per minute until the breaking point was reached and the result, expressed as flexural strength in p.s.i., calculated from the following modulus of rupture formula:

$$S = \frac{MC}{I}$$

where S=the modulus of rupture

M=the moment at the break point

C=the distance from the centroid to the outer surface and

I=the moment of inertia.

Flexural strength of the writing core is influenced by factors other than the composition. Generally, the strength increases with intensive mixing and increased compacting prior to extrusion. The extrusion temperature also influences the flexural strength of the writing core. The optimum extrusion temperature determined for various compositions in the following examples, increased as the proportion of rigid thermoplastic resin component in the mixture was increased. This temperature always remained below the decomposition temperatures of the thermoplastic resinous components.

Beneficially, the rigid plastic component used in this invention is a polymer prepared from a vinyl aromatic compound of the formula AR—CR=CH₂, wherein R is selected from the group consisting of hydrogen and methyl, AR is an aromatic group containing up to ten carbon atoms, and the group —CR=CH₂ is attached directly to a carbon atom of the aromatic ring, which may have chemically combined in the polymer molecule a minor proportion of such substituents as acrylonitrile.

The following examples are illustrative of the present invention but are not to be construed as limiting thereof.

Example 1

20 percent styrene-acrylonitrile copolymer (prepared by the polymerization of about 70 percent styrene and 30 percent acrylonitrile) with a flexural strength of about 17,000 to 19,000 p.s.i. and a melt viscosity of about 14,600 poises when a shearing force of 700,000 dynes/cm.² at 227° C. is applied, 10 percent branched, high pressure polyethylene with a melt viscosity of about 375 poises at 450° F. and 700,000 dynes/cm.² and 70 percent natural flake, amorphous, Mexican graphite (99 percent passing 325 mesh U.S. sieve size) were dry blended and densified by milling on rolls at a temperature of 190-210° C. The mixture was extruded through a 3/8 inch

screw extruder at an extrusion temperature of approximately 180° C. The resulting writing core had a flexural strength of about 8,000 p.s.i. and a hardness, as determined by multiple comparisons with commercial writing lead samples bearing numerical designations, equivalent to No. 3.

Example 2

A mixture of 25 percent styrene-acrylonitrile copolymer, 5 percent branched, high pressure polyethylene and 70 percent graphite, all as defined in Example 1, was blended, densified and extruded as in Example 1 with the extrusion temperature changed to approximately 225° C. The resulting writing core possessed a flexural strength of about 11,500 p.s.i. and a hardness equivalent to No. 4 as determined by multiple comparisons with commercial samples bearing numerical designations.

Example 3

A mixture of 15 percent styrene-acrylonitrile copolymer, 15 percent branched, high pressure polyethylene and 70 percent graphite, all as defined in Example 1, was blended, densified and extruded as in Example 1 with the extrusion temperature changed to approximately 170° C. The resulting writing core possessed a flexural strength of about 7,300 p.s.i. and a hardness equivalent to No. 2½ determined as in the previous examples.

Example 4

A mixture of 25 percent styrene-acrylonitrile copolymer, 12½ percent branched, high pressure polyethylene and 62½ percent graphite, all as defined in Example 1, was blended, densified and extruded as in Example 1, with the extrusion temperature changed to approximately 220° C. The resulting writing core possessed a flexural strength of about 6,800 p.s.i.

Tests of the writing cores described in the preceding examples, both as wood cased pencils and as mechanical pencil leads, demonstrated qualities of writing smoothness, uniformity and visibility of line markings, and core flexural strength that in many instances were superior to commercially available products. The preparation of writing cores in accordance with the invention is completed in a few hours while typical, present day, commercial methods require a week or longer to produce finished leads.

In general, as the graphite component is increased from 70 percent towards a maximum of 80 percent the flexural strength of the product writing core decreases. Reducing the graphite component from approximately 70 percent towards a minimum of 55 percent also results in lower flexural strength. In both cases, the flexural strength may be increased by increasing the ratio of rigid to soft thermoplastic. The following table presents some representative data demonstrating the effects described above.

TABLE I

Percent styrene-acrylonitrile copolymer	Percent branched high pressure polyethylene	Percent graphite	Flexural strength (p.s.i.)
30	15	55	8,400
25	12.5	62.5	8,640
20	10	70	9,100
25	5	70	11,500
30	0	70	13,500

While the foregoing examples and illustrations describe certain embodiments of the invention in consider-

able detail for the purpose of facilitating full and clear understanding, it will be understood that many modifications can be made therein without departing from the scope of the invention.

I claim:

1. A method for making writing cores, in a form ready for use in pencils, which consists essentially in dry blending a mixture of ten to thirty percent of a rigid thermoplastic resin selected from the group consisting of polystyrene and styrene-acrylonitrile copolymers, 1 to 20 percent of a branched, high pressure polyethylene material and 65 to 75 percent natural flake graphite, compacting the mixture at a temperature above the softening point of the rigid thermoplastic resinous material, extruding the so densified mixture through a die with orifices of appropriate diameter and severing the extrudate into required lengths for use in pencils.

2. A composition for writing cores which consists of 65 to 75 percent graphite, 10 to 30 percent styrene-acrylonitrile copolymer and 1 to 20 percent branched, high pressure polyethylene.

3. A composition for writing cores consisting essentially of (a) 55 to 80 percent flake graphite and (b) 20 to 45 percent of organic thermoplastic resinous material consisting of (1) predominantly styrene linear thermoplastic polymer with a flexural strength above 10,000 p.s.i. and (2) a branched, high pressure polyethylene with a melt viscosity of about 300 to 500 poises at 450° F. under a shearing force of 700,000 dynes/cm.².

4. A composition for writing cores consisting essentially of (a) 55 to 80 percent flake graphite and (b) 20 to 45 percent of organic thermoplastic resinous material consisting of (1) a branched, high pressure polyethylene with a melt viscosity of about 300 to 500 poises at 450° F. and 700,000 dynes/cm.² and (2) a copolymer of styrene and acrylonitrile with a melt viscosity of about 10,000 to 20,000 poises at 227° C. and 700,000 dynes/cm.².

5. The method of claim 1 wherein the ratio of rigid thermoplastic resin to polyethylene material is from about 1:1 to 5:1, respectively.

6. A composition for writing cores which consists essentially of from 55 to 80 percent graphite, 10 to 30 percent of an organic thermoplastic resin selected from the group consisting of styrene polymers and styrene-acrylonitrile copolymers, and 0 to 20 percent branched, high pressure polyethylene.

7. A composition for writing cores which consists of 65 to 75 percent graphite, 10 to 30 percent styrene polymer, and 1 to 20 percent branched, high pressure polyethylene.

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3,592,883

MARKING CARBONIZED PENCIL LEADS USING SULFONATED LIGNIN OR AN AQUEOUS SODIUM SALT OF LIGNIN AS A BINDER

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Claims priority, application Japan, Mar. 21, 1968,

43/17,978; June 11, 1968, 43/39,626

Int. Cl. C09d 13/00

U.S. Cl. 264-29

5 Claims

ABSTRACT OF THE DISCLOSURE

Pencil lead is made by mixing 40 to 50 parts of sulfonated lignin or an aqueous sodium salt lignin solution with 30 to 40 parts graphite and 5 to 10 parts of carbon black, kneading the mixture and heating to reduce the moisture content to below 20%. After extruding the mixture into the form of pencil lead and drying the formed articles they are heated to about 500° C. at a very slow rate of 5-10° C. per hour. Once 500° C. has been reached the articles are further heated to above 1000° C. at a faster rate of 30-50° C. per hour in a gaseous phase atmosphere that is inert to the articles, such as nitrogen. The very slow heating rate up to 500° C. is essential to good strength of the carbonized pencil lead. Supplementary binders and plasticizers such as polyvinyl alcohol, tragacanth gum, sodium alginate and carboxymethylcellulose can be added to prevent premature thermal decomposition of the lignin.

This invention relates to a process for making pencil leads.

A lead for a conventional graphite pencil is made by mixing a proper amount of carbon black as a coloring agent with graphite, kneading the mixture with water together with clay as a caking agent, extrusion-molding the mixture and then heating it at 1000 to 1200° C. so as to be sintered. However, such lead is lacking in strength.

This fact has been a very great disadvantage particularly to a very fine lead used for a sharp pencil or lead holder. Further, there is also a process wherein such synthetic resin as vinyl chloride or pitch or the like is used as a caking agent. However, the reaction at the sintering process results in variations such that the hardness will be different in the respective parts. Further, a special solvent is required, a remarkably long time is required for sintering and the complicated production technique requires skill. Such synthetic resin or pitch has so few functional radicals other than alkyl radicals or halogen radicals that the cross-linking reaction in the region of low temperature, in the initial period of sintering, will be insufficient and the molded leads will be fused with each other. Therefore, in order to prevent such fusing, a complicated operation, oxidizing the surface of molded leads in the air or ozone containing air heated about 150° C., is required. Thus the production of the lead is difficult.

An object of the present invention is to provide a process for obtaining fine leads having a breaking strength more than 50 to 100% higher than conventional pencil lead particularly useful for sharp pencils or holders.

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Another object of the present invention is to provide a process for obtaining fine leads which are easy to make and good in the writing touch.

A further object of the present invention is to provide a process for obtaining fine leads cheaply by utilizing a by-product in the production of pulp.

According to the process of the present invention, lignin is dissolved in water or any other proper solvent to form a solution which is thereafter mixed and kneaded with graphite and carbon black; the solvent is evaporated so that the viscosity of the mixture will be suitable for the extrusion molding.

An extrusion molding is operated in 80-95° C.

A wet lead molded in desired diameter is cut, dried in air, heated and baked over 8 hours in an electric furnace up to the maximum temperature 1000-1200° C. in the reducing atmosphere of nitrogen gas.

After being cooled to room temperature, baked lead is dipped in the special oil and heated up to about 200° C. to saturate the micropores of lead with the oil. Thus the process is completed.

For the above described lignin, SP lignin obtained from a waste liquid in the production of pulp by a sulfide process or KP lignin obtained from a waste liquid in the production of kraft pulp are useful. The latter is particularly well suited. An example of its producing process shall be described. First of all, wood chips are treated at a high temperature with a digested solution consisting of sodium hydroxide and sodium sulfide so that about half the amount of the organic components including lignin in the wood may be washed out. In such case, wood fibers are taken out as kraft pulp. The waste liquid thus washed out is blacked viscous liquid containing a large amount of thioglignin and other organic components and inorganic substances. This black liquid is concentrated and as acid is added to it to reduce its pH so that thioglignin of sodium salt may be precipitated. Or a dilute acid is made to further act on the precipitate so that the precipitate may be refined to be of an acid type low in the ash content. It is treated at a high temperature with the addition of sodium sulfite so that a sulfone radical may be introduced into the thioglignin skeleton and is then dried. Such sulfonated lignin is a water-soluble brown powder. When it is dissolved into water and graphite and carbon black are mixed with it, due to the favorable surface active action of said lignin itself, the graphite and carbon black and the lignin itself as a caking agent will easily disperse in water to obtain a uniform mixture. Therefore, the kneading step can be carried out very easily at a high efficiency within a short time.

Further, in case the mixture is dehydrated and extrusion-molded, the slurry viscosity will reduce due to the action of the lignin. Therefore, as described above, it can be easily molded with a comparatively small amount of water. Thus, the drying after the molding is easy and the production efficiency can be increased. Further, lignin has a very large amount of such functional radicals high in the thermoreactivity as -OCH₃, -OH and -COH present in the molecule. Therefore, in the case of baking after the drying, cross-linking will be easily produced in low temperature region in the initial period. That is to say, even in the case it is heated in an inert gas phase, at a temperature below 300° C., the cross-linking reaction will proceed easily. Therefore, there is no fear of causing a fusing phenomenon between the adjacent leads and no

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need of such complicated oxidation operation. Further, as no great weight reduction is caused and the temperature can be elevated comparatively quickly, the operation of the baking step is also easy.

Examples of the present invention shall be explained in the following.

EXAMPLE 1

50 parts of sulfonated lignin are uniformly dissolved into a proper amount of water, then 30 parts of crystal graphite, 20 parts of earth graphite and about 5 parts of carbon black as a coloring agent are put into the solution and the mixture is agitated. It is kneaded with rolls and is at the same time heated to gradually evaporate water. When the water content becomes 15 to 20%, the mixture is put into a lead extruding molder to obtain a lead of any desired diameter. It is then cut into any desired length and has the water content substantially perfectly removed with a hot air dryer. The thus well dried lead is put into a furnace and is heated and baked up to 1000 to 1200° C. for about 8 hours in a reducing atmosphere. After cooling, the lead is taken out and dipped in the oil to saturate the micropores of lead saturate with the oil. A completed pencil lead may be obtained.

EXAMPLE 2

40 parts of sodium salt type lignin or sulfonated lignin mentioned in Example 1 are dissolved in water or a mixed solvent of acetone and alcohol, 30 parts of crystal graphite, 20 parts of earth graphite and about 5 parts of carbon black as a coloring agent are put into the solution and further 10 parts of such natural paste as tragacanth gum are mixed into it and a pencil lead is made by the same process as in Example 1. In such case, the natural paste is to make the molding of the lead easy.

The graphite pencil lead made by such producing process as is described above is so good in the writing touch as to be smooth in writing and has a very high breaking strength. For example, the pencil lead of the same hardness as of a conventional lead having a transverse strength of 8000 to 11,000 g./mm.² can give a strength of 12,000 to 20,000 g./mm.².

According to the present invention, when the temperature elevating velocity for baking the lead is reduced to 5 to 10° C. per hour so that the lead may be heated very gradually (and also a proper paste is mixed into the caking agent lignin) the quick thermal decomposition of the lignin in region of a low temperature can be prevented, the residual carbon can be increased and the breaking strength can be more remarkably increased.

In the present process, after such natural or synthetic paste as, for example, tragacanth gum or polyvinyl alcohol is added to the lignin, graphite and carbon black admixture, the mixture is agitated, kneaded, so that the water content may be reduced to about 10 to 20% and then formed into a lead of any desired diameter with an extruding molder or the like. This lead is dried in air, put into the electric furnace and heated first very gradually up to 500° C. at a temperature elevating velocity of 5 to 10° C. per hour. That is to say, 500° C. is reached by taking more than 60 to 100 hours. Then the temperature elevating velocity is increased to about 30 to 50° C. per hour to heat and bake the lead up to 1000 to 1200° C. The lead coming through such baking step is dipped in an oil bath to be impregnated with oil so that a completed lead may be obtained.

When the aforementioned paste is added to the lignin solution, the molding will become easy, the raw lead before being baked will be hard to break and the yield will increase. It is therefore very effective. Further, such paste addition prevents premature decomposition of the lignin occurring in a low temperature region by uniformly reacting of such with functional groups of lignin, also the amount of residual carbon is increased by the recondenation of low molecular weight decomposition products and

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therefore acts on growth of the bonded carbon structure contributing to effective sintering. The paste employed is a substance of a long chain molecular such as cellulose or a substance having many hydrogen bonds and desirably the paste is water-soluble. Such natural, synthetic or semi-synthetic paste as for example, tragacanth gum, sodium alginate, poly-sodium acrylate, carboxymethylcellulose or polyvinyl alcohol are so reactive with lignin and so unlikely to decompose as to be able to be effectively utilized in the process of the present invention.

Further, in the case of mixing graphite and carbon black with a lignin solution (to which such proper paste mentioned above has been added, molding the mixture and drying and baking it) when the temperature is very gradually elevated at a velocity of 5 to 7° C. per hour in the range from the room temperature to about 500° C., the quick reaction in a low temperature region is prevented, the rate of residual carbon is increased and the bonded carbon structure contributing to the sintering is sufficiently grown, the breaking strength can be remarkably increased. That is to say, as the reactivity in the low temperature region by the functional radicals of the lignin and paste is well elevated and a long time is taken, the uniformity will improve, the residual carbonaceous substances forming the structure will increase, therefore the sinterability will improve and the strength of the lead will increase. For example, in case the temperature is elevated at a velocity of 50° C. per hour from the room temperature to 500° C., fine cracks will be produced and it will be difficult to obtain a breaking strength above about 12,000 to 20,000 g./mm.². On the other hand, if the temperature is gradually elevated at a reduced velocity of 10° C. per hour in the range up to 500° C. as described above, such cracks will be prevented and a breaking strength of 20,000 to 28,000 g./mm.² can be obtained. If this temperature elevating velocity is further reduced to 5° C. per hour, the breaking strength will become 23,000 to 30,000 g./mm.² and the lower limit will increase. That is to say, when the temperature elevating velocity is reduced to be below 10° C. per hour, the breaking strength will remarkably increase and, when it is reduced to be lower, the lower limit of the breaking strength will gradually increase. Therefore, in the present invention, the temperature elevating velocity is made less than 10° C. or particularly 5 to 7° C. per hour from the room temperature up to about 500° C. and is made comparatively higher to be about 30 to 50° C. per hour from 500° C. up to 1,000 to 1,200° C. in baking.

An example of the above mentioned process is shown in the following.

EXAMPLE 3

A material solution of a composition of 40 parts by weight of lignin sulfonate, 10 parts by weight of polyvinyl alcohol, 10 parts by weight of ethylene glycol and 100 parts by weight of water is prepared, 40 parts by weight of graphite and 10 parts by weight of carbon black are mixed with it and the mixture is well agitated, is properly evaporated and is well kneaded with mixing rolls. At the same time, the mixture is heated to evaporate water contained in it. When the water content becomes 10 to 15%, a lead of any desired size is formed of the mixture with an extruding molder. The lead is wound up, cut into a proper length, dried and then put into a furnace and baked up to 500° C. elevating the temperature 5° C. per hour. Then the lead is heated up to 1,100° C. at an increased temperature elevating velocity of 30° C. per hour and cooled naturally. The lead is taken out of the furnace, and dipped in an oil bath to be impregnated with oil and to be completed. The thus obtained pencil lead has a breaking strength of 23,000 to 28,000 g./mm.² as described above and is good in the writing touch.

What is claimed is:

1. A process for making pencil leads comprising the steps of dissolving from about 40 to 50 parts sulfonated

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lignin or lignin in sodium salt form in water, adding from about 30 to 40 parts graphite of the type normally used for producing pencil leads and from about 5 to 10 parts carbon black to said solution, kneading said mixture with a mixer while heating to reduce the water content to below about 20%, molding the mixture with an extruding molder, drying the resultant molded article to remove the water content, thereafter baking said article by gradually raising the temperature at a heating rate of from about 5-10° C. per hour to a temperature of about 500° C. and thereafter increasing the heating rate to about 30-50° C. per hour to a temperature of at least about 1,000 C. in a gas phase inert to said article, thereby producing a pencil lead of good hardness and strength.

2. The process of claim 1 wherein the heating rate to about 500° C. is about 7° C. per hour and the heating rate between 500° C. and at least about 1,000° C. is about 50° C. per hour.

3. The process of claim 2 wherein 50 parts sulfonated lignin is employed with 50 parts graphite.

4. The process of claim 3 wherein a substance taken from the group consisting of tragacanth gum, sodium alginate, polysodium acrylate, carboxymethylcellulose,

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or polyvinyl alcohol is added to the solution of sulfonated lignin.

5. The process of claim 3 wherein the baking is carried out in an atmosphere of nitrogen.

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106-19, 26, 123

[54] THERMOPLASTIC BINDERS FOR CONTINUOUSLY PRODUCED LEADS FOR PENCILS, COPYING PENCILS AND COLOURED PENCILS

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[58] Field of Search 260/41 R, 41 C, 28.5 AV; 106/19

[56]

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[57]

ABSTRACT

Leads for writing purposes comprising a graft polymer of an ethylene/vinyl acetate copolymer, a vinyl chloride and a graft copolymer of a styrene and an acrylonitrile type monomer onto a butadiene polymer and graphite or a scouring agent.

4 Claims, No Drawings

**THERMOPLASTIC BINDERS FOR
CONTINUOUSLY PRODUCED LEADS FOR
PENCILS, COPYING PENCILS AND COLOURED
PENCILS**

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

This application is a continuation of application Ser. No. 147,648 filed May 27, 1971 and now abandoned, which, in turn, was a continuation of application Ser. No. 755,779 filed Aug. 28, 1968 and now abandoned.

This invention relates to thermoplastic binders for continuously produced leads for pencils, copying pencils and coloured pencils, and to the leads themselves.

Hitherto, two methods have been used for manufacturing leads for writing purposes, namely:

1. The production of ordinary pencil leads with graphite as the colouring agent.

2. The production of leads for coloured pencils and copying pencils with special dyes as the colouring agents.

The first of these two processes is conventionally carried out as follows:

A mixture of powdered graphite, suspended clay and water is first intensively mixed and then extruded under high pressure through a die. The resulting strand of lead, suitably supported, is dried and baked at a suitable temperature and under suitable climatic conditions.

Apart from the lengthiness of this process, due to the complicated drying and tempering operations, it has the following disadvantages:

a. Considerable difficulties are involved in maintaining a uniform thickness of the lead,

b. Cracks often develop during drying, despite all the precautions taken to prevent this, and

c. Even after drying, the leads are readily broken so that they can only be produced in limited lengths.

The second of the two processes for the production of coloured leads has been substantially simplified over a period of time by the following procedure:

A mixture of dye, filler, lubricant, binder and of a monomeric vinyl compound, for example vinyl acetate or styrene, is homogenised under heat in a kneading machine in the presence of an organic peroxide, and the resulting moulding composition is extruded through a single-screw extruder to form a strand of lead after it has been additionally pre-plasticised at elevated temperature. In addition to the vinyl polymer thus obtained, which acts also as a binder, a wide variety of cellulose esters have heretofore been used as special binders. Inorganic materials, for example, clay or talc, are primarily used as fillers.

Although a process of this kind may be eminently suitable for the production of coloured leads, it cannot be used for the production of ordinary leads because inorganic fillers or dyes such as graphite can only be used in quantities of up to about 50 percent by weight, based on the mixture as a whole. With higher graphite and filler contents, the resulting strand of lead increases in fragility and is deprived of its homogeneity so that the writing composition can no longer be extruded. This limit to the filler content is explained by the nature of the hitherto used binders which, although

partly thermoplastic, are only able to absorb a limited quantity of filler and dye and which, when used in fairly large quantities, lose their binding power owing to their resin-like character. To produce leads for pencils, however, the composition should advantageously have a relatively high graphite content, because the quality of the pencil lead is judged by its chalking capacity, which in turn is governed by the amount of colouring agent (for example graphite) present.

Although this state of affairs has been appreciated for some considerable time in writing lead technology, all attempts to find a binder suitable for the continuous production of leads with a filler content in excess of 50 percent by weight have so far failed.

It has now been found that this can be done by using the following polymers or polymer combinations as the binders:

A. 1 to 100 parts by weight of a graft polymer of

a. 25 to 85 percent by weight of an ethylene/vinyl acetate copolymer with a vinyl acetate content of from 20 to 70 percent by weight and preferably from 30 to 55 percent by weight as the base, and

b. 75 to 15 percent by weight of grafted-on vinyl chloride; this graft polymer may also be replaced either wholly or in part by copolymer (a); and

B. 99 to 0 parts by weight of a graft polymer of

a. 5 to 60 percent by weight of a butadiene polymer with optionally up to 30 percent by weight of copolymerised styrene, acrylonitrile, isoprene or the lowest alkyl esters of acrylic or methacrylic acid,

b. 95 to 40 percent by weight of polymerised styrene and acrylonitrile in a ratio by weight from 95:5 to 50:50 wherein these two monomer components may be replaced either wholly or in part by their respective alkyl derivatives; alternatively one or both may be replaced either wholly or in part by methyl methacrylate;

all or part of the styrene or acrylonitrile having been polymerised in the presence of the butadiene polymer and the residual component of styrene and acrylonitrile added in the course of a partial graft polymerisation reaction, optionally even in separately copolymerised form.

This discovery was completely surprising and could not be derived from the prior art. It is possible, by using the aforementioned polymers or polymer combinations, to produce, for example, writing leads containing up to 90 percent by weight of graphite and which can be extruded through a conventional extruder to form a continuous strand of lead of uniform thickness and of any length, without any breakages in the strand of lead. In addition, it is possible by varying the binder, lubricant, filler and dye contents to adjust any required degree of hardness without in any way detrimentally influencing the procedure.

In one particular preferred embodiment, the following polymer combination is used as a binder in particular for the continuous production of pencil leads:

A. 1 to 100 parts by weight of a graft polymer of

a. 25 to 85 percent by weight of an ethylene/vinyl acetate copolymer with a vinyl acetate content of from 20 to 70 percent by weight, and preferably 30 to 55 percent by weight, and

b. 75 to 15 percent by weight of grafted-on vinyl chloride; and

B. 99 to 0 parts by weight of a graft polymer of

- a. 5 to 60 percent by weight of a butadiene polymer with optionally up to 30 percent by weight of copolymerised styrene,
- b. 95 to 40 percent by weight of polymerised styrene and acrylonitrile in a ratio by weight of 95:5 to 50:50 wherein these two monomer components may be replaced either wholly or in part by their respective alkyl derivatives, or alternatively one or both of them may be replaced either wholly or in part by methyl methacrylate;

all or part of the styrene and acrylonitrile having been polymerised in the presence of the butadiene polymer and the residual components of styrene and acrylonitrile, optionally in separately copolymerised form, having been added in the course of a partial graft polymerisation reaction.

According to another preferred embodiment, the graft polymer component (a) and the graft polymer component (b) are employed in a weight ratio of from 80:60 to 20:40.

The polymers, copolymers and graft copolymers required for the binders used according to the invention are obtained by conventional processes. Thus, German Patent Specification No. 1,126,613, for example, describes the preparation of ethylene/vinyl acetate copolymers, whilst Belgian Patent Specification No. 510,460 provides full details of suitable graft polymers of vinyl chloride on ethylene/vinyl acetate copolymers. The same also applies as regards the polymer component (B) which is prepared in accordance with the procedure generally employed for acrylonitrile/butadiene/styrene polymers (ABS-polymers). Details of the procedure adopted for the preparation of ABS-polymers may be found, for example, in British Patent Specification No. 794,400 and in German Patent Application No. F 44,156 IVd/39c. It should be emphasised in this respect, however, that the preparation of polymers such as these is not necessarily restricted to an emulsion polymerisation process because, on the other hand, it is also possible to prepare ABS-polymers by suspension or mass bead polymerisation processes.

In another modification of the process according to the invention, it is also possible to replace the graft polymer component (B) of the binder combination according to the invention by a so-called ABS-copolymer. Products of this kind are prepared by mixing a rubber-like copolymer, for example, a butadiene/styrene copolymer, with a resin-like copolymer, for example a styrene/acrylonitrile copolymer, in suitable proportions.

The butadiene polymer used as graft base in the preparation of graft polymer component (B) is initially restricted to a comonomer component of 30 percent by weight. When ethyl acrylate or butyl acrylate or alkyl vinyl ethers are used, this comonomer component may, however, be increased to from 50 to 70 percent by weight, without substantially affecting the elastomeric properties of the graft base.

The writing lead composition required for carrying out the continuous lead manufacturing process is produced by introducing polymer component (A) or polymer components (A) and (B) into a mixer to which plasticisers, bonding agents and lubricants, a colouring agent and, optionally, a filler are simultaneously added. If polymer component (A) is a graft polymer containing vinyl chloride, a PVC stabiliser has also to be

added. The usual PVC stabilisers (PVC = polyvinyl chloride), for example basic lead sulphates, barium/cadmium soaps or organotin compounds, may be used for this purpose. Suitable mixing units include, for example, mixing rolls, internal kneaders, high speed mixers or fluid mixers.

Initially, the quantities in which the additives are used are governed solely by the quantities in which the colouring agent and the binder are employed. By virtue of the properties of the binder used according to the invention, a high proportion of the colouring agent may be employed, in which case the quantities of the other additives or fillers are reduced accordingly.

In addition, it is possible, by varying the type and quantitative ratio of polymer components (A) and (B), to influence both the properties and the hardness of the leads without in any way affecting the possibility of adjusting the hardness of the leads by means of other additives. When the binder according to the invention is used, the content of colouring agent may be increased, depending upon the type of lead (ordinary lead or coloured lead) to up to 90 percent by weight, based on the mixture as a whole, without in any way affecting the possibility of manufacturing a continuous lead.

The dyes normally used in writing lead technology, for example graphite, inorganic or organic pigments and pure organic dyes, may be used as the colouring agent, providing their thermal stability is such as to allow extrusion. The following are mentioned by way of example: iron oxides, cadmium sulphides and selenides, carbon blacks, chromium oxides and phthalocyanines.

Suitable bonding agents and lubricants include the substances normally used for this purpose in the production of writing leads, for example, fats and waxes, alkali metal and alkaline earth metal salts or stearic acid, stearyl alcohol and, in another preferred embodiment of the process, the bis-stearyl amide of ethylene diamine.

When the binder or binder combination according to the invention is used, in this particular context polymer component (A), it is also possible to add fairly small quantities of a plasticiser, for example a phthalic acid, adipic acid or phosphoric acid ester, or a reaction product of a fairly long chain alkyl sulphonic acid with a monohydric or polyhydric phenol.

In order to adjust the required degree of hardness, the hardeners normally used in the manufacture of writing leads, for example, kaolin or powdered quartz, may be added.

The writing lead composition according to the invention may be extruded in conventional single-screw or twin-screw extruders. In order to obtain uniform distribution, however, it has proved to be of advantage to use a twin-screw extruder. The processing temperatures used are governed solely by the type of colouring agent employed and by the composition of the binder used according to the invention. As a rule, processing temperatures in the range from 170° to 200°C. are preferred.

It is possible by applying the process according to the invention and by using the binder according to the invention continuously to produce strands of ordinary lead or coloured lead of any length and of constant diameter which combine high breaking strength with excellent chalking properties. The leads may be produced in all the thicknesses normally used for lead pencils and

coloured pencils or art pencils. The diameter and shape of the lead are governed solely by the shape and diameter of the nozzle attached to the processing machine. Although an extrusion die 2.3 mm. in diameter is normally used for this purpose, it is also possible to use an extrusion die with a diameter of, for example, 10 mm., or a die with a triangular or rectangular outlet. In addition, it is possible to vary the composition of the binder used according to the invention in such a way as to obtain leads of any hardness. The process according to the invention and the binder according to the invention are illustrated by the following Examples. Unless otherwise stated, the parts and percentages indicated are parts and percentages by weight.

EXAMPLES 1 - 6

The following constituents are introduced into and homogenised in a high speed beater mill:

	Example					
	1	2	3	4	5	6
Polymer component A (parts)	180	160	120	80	40	60
Graft polymer of 40% by weight of vinyl chloride, 23% by weight of vinyl acetate, 37% by weight of ethylene						
Polymer component B (parts) comprising	20	40	80	120	160	180
a) 30% by weight of a graft polymer of 35% by weight of styrene and 15% by weight of acrylonitrile on 50% by weight of polybutadiene						
b) 70% by weight of styrene/acrylonitrile copolymer 70:30, $\eta_i = 0.60$ (0.5% solution in dimethyl formamide at 20°C.)						
Alkyl sulphonic acid ester (parts) of phenol with an alkyl radical of 15 carbon atoms	10	10	10	10	10	10
Barium cadmium laurate (parts)	10	10	10	10	10	10
Ethylene diamine bis-stearyl amide (parts)	40	40	40	40	40	40

After thoroughly mixing, 750 parts of graphite are added in each instance, and the mixture as a whole is transferred to a laboratory ball mill after further homogenisation. The mixtures are each ground in this ball mill for 30 minutes and then extruded by means of a twin-screw extruder through an extrusion die. The processing temperature is 180°C. The resulting strand of lead is drawn off and rolled up or cut to lengths, depending upon the degree of hardness adjusted. Despite their high graphite content (74.2 percent by weight), the finished leads show a uniform diameter of 2.2 mm. and a high breaking strength. Their chalking properties are excellent.

EXAMPLE 7

The procedure is as described in Example 1, except that in this instance polymer component B is not added. Instead, the quantity in which polymer component A is used is increased to 200 parts by weight. A strand of lead of outstanding flexibility and high breaking strength is obtained.

EXAMPLE 8

150 parts by weight of an ethylene/vinyl acetate copolymer with a vinyl acetate content of 45 percent by weight and a Mooney viscosity of 20 (ML-4'-value) are

compacted to form a sheet on mixing rolls at a temperature of 140°C. Following the addition of 50 parts by weight of the polymer component B already described in Example 1, the following constituents are added after continued rolling:

10 parts by weight of benzyl octyl adipate
40 parts by weight of calcium stearate, and
750 parts by weight of graphite.

The rolled sheet is drawn off and granulated. The granulate thus obtained is further processed as described in Example 1. The finished strand of lead has a high breaking strength and excellent chalking properties.

EXAMPLE 9

The following components are homogenised on mixing rolls:

200 parts by weight of an ethylene/vinyl acetate co-

polymer with a vinyl acetate content of 45 percent by weight (ML-4' = 20),
40 parts by weight of the bis-stearyl amide of ethylene diamine,
10 parts by weight of dibutyl phthalate, and
750 parts by weight of graphite

The product is further processed as described in Example 8, the only difference being that component B is not added.

Following granulation, a strand of lead of outstanding flexibility is again extruded through a twin-screw extruder.

EXAMPLE 10

The following components are introduced into a high speed beater mill:

120 parts by weight of the polymer component (A) already described in Example 1,
80 parts by weight of the polymer component (B) described in Example 1,
10 parts by weight of the alkyl sulphonic acid ester of phenol, having an alkyl radical of 15 carbon atoms,
10 parts by weight of barium cadmium laurate,
40 parts by weight of calcium stearate.

After thorough mixing, the following components are added:

400 parts by weight of a calcium sulphide selenide pigment (Cadmpurrot 400 [a registered trade mark of Farbenfabriken Bayer AG]),
400 parts by weight of talc.

After intensive grinding in a ball mill, the lead composition is again extruded through a twin-screw extruder to form a uniform strand of lead 5 mm. in diameter. A red lead with outstanding chalking properties, high flexibility and equally high breaking strength is obtained.

EXAMPLE 11

A lead of the following composition is prepared in accordance with the procedure described in Example 2:

160 parts by weight of the polymer component (A) already described in Example 2,
40 parts by weight of a graft polymer of 80 percent by weight of styrene/acrylonitrile in a weight ratio of 70:30 on 20 percent by weight of a butadiene/styrene copolymer in a weight ratio of 80:20,
10 parts by weight of barium cadmium laurate,
10 parts by weight of dibutyl phthalate,
40 parts by weight of the bis-stearyl amide of ethylene diamine,
750 parts by weight of graphite.

The lead composition according to the invention is again extruded through a twin-screw extruder as described in Examples 1 to 6. A strand of lead of high breaking strength and excellent chalking properties is also obtained with a composition of this kind.

EXAMPLE 12

If the polymer component (B) of Example 4 is replaced by a graft polymer of 50 percent by weight of styrene/acrylonitrile on 50 percent by weight of polybutadiene, a strand of lead of outstanding elasticity is obtained after the moulding composition has been worked up as described in Examples 1 to 6.

We claim:

1. A pencil lead comprising an extruded intimate admixture of 50 to 90 percent by weight of graphite or other pencil coloring agent capable of chalking and 50 to 10 percent by weight of a binder comprising a mixture of

A. 1 to 100 parts by weight of a graft copolymer of 25 to 85 percent by weight of an ethylene/vinyl acetate copolymer having a vinyl acetate content of from 20 to 70 percent by weight as grafting substrate and 75 to 15 percent by weight of grafted on vinyl chloride,

B. 99 to 0 percent by weight of a graft copolymer or a graft polymer-copolymer mixture comprising

a. 5 to 60 percent by weight of a butadiene homopolymer or a copolymer of butadiene and up to 30 percent by weight of copolymerized styrene and

b. 95 to 40 percent by weight of (1) polymerized styrene, methylmethacrylate or a mixture thereof and (2) acrylonitrile methylmethacrylate or a mixture thereof in a ratio by weight of 95:5 to 50:5 wherein (b) is at least partially grafted on (a) and any remainder of (b) is present as the copolymer in said graft polymer-copolymer mixture.

2. The pencil lead of claim 1 wherein (A) has a vinyl acetate content of from 30 to 55 percent by weight.

3. The pencil lead of claim 1 wherein graphite is the pencil coloring agent capable of chalking.

4. The pencil lead of claim 1 wherein (A) comprises a graft polymer of 40 percent by weight of vinyl chloride, 23 percent by weight of vinyl acetate and 37 percent by weight of ethylene and (B) comprises a mixture of 30 percent by weight of a graft polymer comprising 30 percent by weight of styrene and 50 percent by weight of acrylonitrile grafted on 50 percent by weight of polybutadiene and 70 percent by weight of a copolymer of styrene and acrylonitrile in a ratio of 70:30.

* * * * *

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3,834,910

PENCIL LEAD

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2 Claims

ABSTRACT OF THE DISCLOSURE

A pencil lead which consists essentially of a powdery coloring agent bonded by an uncured epoxy resin of the 2,2 - bis(4' - hydroxyphenyl)propane/epichlorohydrine which is solid at room temperature.

This invention relates to a pencil lead. More particularly, the invention relates to a pencil lead consisting essentially of a powdery coloring agent bonded by a specific epoxy resin, which has a sufficiently practical strength at a hardness of grade H or HB and is excellent in graphic characteristics.

In general, pencil leads are prepared by bonding powdery coloring agents with binders. For instance, in the case of commercially available graphite leads, natural graphite powder is used as the coloring agent and natural clay is used as binder for bonding the graphite powder. More specifically, since a clay which has contained a suitable amount of water exhibits plasticity, by utilizing this property, a mixture of graphite powder and such clay is extruded under pressure from small holes to mold it into the lead-like form, and then it is dried and fired at about 1100° C. to sinter the clay and impart a desired strength to the product lead.

Pencil leads prepared by such conventional method have the following two fatal defects.

(1) Since a natural clay is used as a binder, unevenness in quality is great and it is difficult to obtain products which are completely uniform in hardness, diameter and the like. Further, in the case of leads having a high hardness (harder than grade 3H), clay particles tend to scratch on paper at the time of writing and it frequently happens that writing cannot be conducted smoothly.

(2) Since the products are obtained inevitably through the firing step, it is impossible to obtain continuous leads having an endless length.

The above defect (1) can readily be understood from the fact that in commercially available pencils, the hardness or lead diameter differs more or less in pencils of the same grade.

The above defect (2) has a great significance when a casing of the pencil is formed from a plastic material or its foamed product. The reason is as follows:

Natural special woods such as incense cedar produced in California, U.S.A., have heretofore been used as materials for casings of pencils, but the recent rise in price of such woods has invited movements of substituting a plastic material or its foamed product for such special wood in the art of pencil manufacture. In this case, if slats are formed from a plastic material one by one as in the case of wooden casings, the manufacturing cost becomes extremely high and the object of the substitution cannot be attained. For this reason, when a plastic material is used for formation of pencil casings, a technique similar to the technique adopted for the manufacture of coated electric wires is employed. Namely, it has been tried to obtain a pencil of an endless length at a stroke by coating the periphery of a lead with a plastic material or its foamed product with use of an apparatus resembling a die customarily used for coating electric wires. However,

in order to make such process practically workable, it is indispensable that leads should be continuous and have an endless length.

In order to provide pencil leads free of the above defects, various attempts have been made to utilize plastics as binders instead of clays, but none of them have succeeded in giving satisfactory results. For instance, the specification of U.S. Pat. No. 3,262,904 teaches the use as a binder of a mixture of polystyrene and high pressure polyethylene or a mixture of an acrylonitrile/styrene copolymer resin and high pressure polyethylene. However, as is disclosed in Examples of the above specification, the lead of No. 2½ grade (corresponding to grade F) has a bending strength of only 7300 p.s.i. (5110 g./mm.²), and, from the viewpoint of the strength the lead proposed in the above specification cannot be a practically satisfactory substitute for the conventional product. Further, the specification of U.S. Pat. 3,360,489 proposes the use as a binder of a polymer having a colloidal particle size, such as PVC latex. However, when such polymer of the latex form is employed, though the firing step can be omitted, troublesome operations should be conducted for removing water from such polymer. We reproduced the teachings of the above specification to determine the utility of such polymer of the latex form and found that, contrary to the disclosures of the above specification, it was impossible to obtain leads of a hardness of grade H or HB having a practically satisfactory strength. Again, it has been proposed to use as a binder a thermosetting resin such as furan resin or melamine resin. However, in each case there are obtained only leads of a very high hardness and it is impossible to obtain pencil leads of a hardness of grade H or HB.

As described above, according to conventional techniques using plastic materials as binders for powdery coloring agents, it has been impossible to obtain pencil leads of practically sufficient quality as regards the hardness of grade H or HB.

Accordingly, it is a primary object of this invention to provide pencil leads consisting essentially of a powdery coloring agent bonded by a plastic material binder, which exhibits satisfactory properties at a hardness of grade H or HB.

We have found that this object of this invention can be attained when an uncured epoxy resin of the 2,2-bis(4'-hydroxyphenyl)propane/epichlorohydrin type which is solid at room temperature is used as a binder for a powdery coloring agent.

By the term "an uncured epoxy resin of the 2,2-bis(4'-hydroxyphenyl)propane/epichlorohydrin type which is solid at room temperature" is meant an epoxy resin of the 2,2-bis(4' - hydroxyphenyl)propane/epichlorohydrin type which is not incorporated with a curing agent and is in the thermoplastic state and has an average molecular weight of from about 700 to about 7000, preferably from about 1000 to about 6000. In general, when an epoxy resin is used as a binder, a three-dimensional cross-linked structure is formed in the resin by curing it with a curing agent such as amines and acid anhydrides. In contrast to such customary manner of the use of epoxy resins, this invention is characterized in that an epoxy resin of the 2,2 - bis(4'-hydroxyphenyl)propane/epichlorohydrin type is used as a binder in the uncured state not incorporated with any curing agent. In the instant specification, such epoxy resin will sometimes be referred to merely as "epoxy resin."

As commercially available epoxy resins to be used preferably in this invention, there may be mentioned, for example, Epikote 1004 (molecular weight=about 1400; melting point=96-104° C.), Epikote 1007 (molecular weight=about 2900; melting point=122-131° C.), Epikote 1009 (molecular weight=about 3750; melting

point=144–158° C.), Epikote 1010 (molecular weight=about 5000; melting point=155–165° C.), Araldite 6084 (melting point=95–105° C.), Araldite 6097 (melting point=125–135° C.), Araldite 6099 (melting point=145–155° C.), DER 664 (melting point=95–105° C.), DER 668 (melting point=120–140° C.) and DER 669 (melting point=135–155° C.) Epikote, Araldite and DER are trade names for products of Shell International Chemicals Corporation, Ciba Products Company and Dow Chemical Company, respectively.

All of powdery coloring agents that have been used for the preparation of graphite leads and colored leads, such as natural crystalline graphite, natural amorphous graphite, artificial graphite and various organic pigments, may be used in this invention as the powdery coloring agent.

In a preferable embodiment of preparing a graphite lead according to this invention, graphite powder, finely divided powder of the above-mentioned epoxy resin and, if desired, a hardness adjuster are blended by means of a mixer, the resulting powdery mixture is dried at about 80° C. and melt-extruded from an extruder in which the maximum cylinder temperature is adjusted within the range of from 140 to 180° C., the extruded strands are hot-cut into pellets, and finally the pellets are extrusion-molded by means of a lead-forming extruder at the end of which a die having holes of a diameter of 2 mm. is mounted. Thus, graphite leads are obtained.

The hardness adjuster may be used in an amount necessary for imparting the desired hardness to the product lead. When the hardness adjuster is not employed, the resulting graphite lead has a hardness of 7H or 8H. Metal soaps are usually employed as such hardness adjuster. Among metal soaps, calcium and aluminum salts of stearic acid and lauric acid are especially useful because they are non-toxic.

Examples of the mixing ratio of the graphite powder, epoxy resin powder and hardness adjuster are as follows:

	Mixing ratio (percent by weight)		
	Graphite powder	Epoxy resin	Hardness adjuster
Graphite lead of HB hardness.....	70	12	18
Graphite lead of H hardness.....	70	18	12
Graphite lead of 4H hardness.....	70	20.5	9.5
Graphite lead of 7H hardness.....	65	35	0

In the case of graphite leads of a hardness of grade HB or H, it is possible to heighten the graphite concentration up to about 75% by weight. It is convenient to conduct the melt-kneading of the starting material mixture in an extruder in a manner as described above, but it is also possible to employ a Banbury mixer or roll mill to effect the melt-kneading of the starting material mixture. Further, a part of graphite may be replaced by other black pigment, and various additives customarily used for the production of molded articles of plastics, such as stabilizers and fillers, may be incorporated into the starting material mixture.

In another embodiment of this invention colored leads are prepared. In this embodiment, organic pigments are used as the powdery coloring agent. These pigments are selected from organic pigments which have no toxicity, can give a desired color on writing and have a heat resistance sufficient to withstand high temperatures adopted at the molding step. In the case of graphite leads, graphite powder incorporated as the powdery coloring agent acts also as a filler giving rigidity to the product. In the case of colored leads, however, it is necessary to incorporate a filler (white color) exhibiting such rigidity-imparting action. Use of talcum powder is most suitable for this purpose. In the case of colored leads as well as in the case of graphite leads, in order to reduce the hardness, it is necessary to incorporate as a hardness adjuster a metal soap as calcium stearate.

Preferable examples of the composition of the starting material mixture for a colored lead are as follows:

Mixing Ratio (on the weight basis)

Organic Pigment	7–10
Epoxy Resin	16–20
Calcium Stearate	13–16
Talcum Powder	55–65

For the preparation of colored leads from such starting materials, an extrusion molding method such as described above with respect to graphite leads may be conveniently adopted. As in the case of graphite leads, various additives customarily used in the production of molded articles of plastics may also be incorporated in the above starting material mixture to be used for the preparation of leads.

In this invention, in order to reduce the manufacturing cost, up to 50% by weight of the epoxy resin may be replaced by other thermoplastic resin. As such thermoplastic resin, there may be employed acrylonitrile/styrene copolymer resin and ethyl cellulose. When more than 50% by weight of the epoxy resin is replaced by such thermoplastic resin, the resulting lead has a strength as the lead taught in the above-quoted specification of U.S. Pat. 3,360,489. Therefore, it is not preferred to incorporate such thermoplastic resin in such a great amount.

This invention will now be illustrated in more details by reference to non-limitative Examples.

EXAMPLE 1

This Example illustrates the preparation of graphite lead of a degree of hardness HB.

1200 g. of an epoxy resin (Epikote 1010 manufactured by Shell International Chemicals Corporation; molecular weight=about 5000; melting point=155–165° C.) which had been ground to pass through a 20-mesh sieve, 7000 g. of natural crystalline graphite (average particle size=6 μ) and 1800 g. of calcium stearate were well mixed in a Henschel mixer, and the mixture was dried at 85° C. for 5 hours. Then, the mixture was fed to an extruder at the front end point of which a die having holes of a diameter of 3.0 mm. was mounted, and the melt-extrusion was conducted at a cylinder temperature of 130° C. (at the rear)—140° C. (at the front) and at a die temperature of 130° C. The extruded strands were hot-cut into pellets having a length of 4–6 mm.

The so obtained pellets for formation of leads were fed to a lead-molding extruder at the end point of which a die having pores of a diameter of 2.0 mm. was mounted, and were continuously extruded at a cylinder temperature of 140° C. (at the rear)—145° C. (at the center)—150° C. (at the front) and at a die temperature of 140° C. The extrudate was continuously wound onto a drum of a diameter of 1.5 m. to obtain a graphite lead of an endless length having a diameter of 2.0 mm.

When the hardness of the resulting graphite lead was compared with those of commercially available graphite leads, it was found that the hardness was of grade HB. The bending strength of the so obtained graphite lead as measured according to the method of JIS S-6005-1971 after one week's conditioning was 6400 g./mm.². This strength-measuring method according to JIS S-6005-1971 is conducted as follows:

A lead is supported by two points, and a concentrated load is laid at the central point between the two supporting points. The concentrated minimum load that can break the lead is measured, and the flexural strength is calculated by the following formula:

$$f = \frac{8PL}{\pi d^3}$$

wherein f designates the bending strength (g./mm.²), P stands for the minimum concentrated load (g.) laid on the center that can break the lead, L indicates the dis-

tance (mm.) between the two supporting points (usually adjusted to 60 mm.), and *d* designates the diameter of the lead.

Conventional endless graphite leads prepared by employing plastics as binders have a bending strength of 3500 to 5000 g./mm.², and the minimum bending strength passing the test standard stipulated by JIS is 500 g./mm.² in the case of a lead of a hardness of grade HB. In view of the foregoing, it will readily be understood that the product of this invention obtained in this Example is very excellent. In fact, when it was actually used for writing, it was not broken at all.

A graphite lead was prepared by repeating the above procedures except that 500 g. of an acrylonitrile/styrene copolymer (Tyrl manufactured by Asahi Dow Chemicals) and 700 g. of the epoxy resin were used instead of 1200 g. of the epoxy resin. Namely, 500 g. of the epoxy resin was replaced by the same amount of the above copolymer. The bending strength of the so prepared graphite lead was 6200 kg./cm.².

For comparison, a graphite lead was prepared by repeating the above procedures except that 1200 g. of the above acrylonitrile/styrene copolymer was used instead of 1200 g. of the epoxy resin. The bending strength of the so prepared graphite lead was 5000 g./mm.². A lead of a bending strength of such low level has no high practical value, because the point portion of the lead tends to be broken on writing.

EXAMPLE 2

This Example illustrates the preparation of a graphite lead of a hardness of grade H.

A graphite lead was prepared in the same manner as in Example 1 by changing conditions in the following three points (1) to (3):

(1) Starting Materials:

Epoxy resin (Epikote 1009 manufactured by Shell International Chemicals Corporation; molecular weight=about 3750; melting point=144-158° C.)—1800 g.

Graphite powder—7000 g.

Calcium stearate—1200 g.

(2) Strands Extrusion Conditions:

Cylinder temperature—160° C. (at the rear)—170° C. (at the front)

Die temperature—160° C.

(3) Lead-Molding Conditions:

Cylinder temperature—150° C. (at the rear)—155° C. (at the center)—160° C. (at the front)

Die temperature—150° C.

The resulting graphite lead had a bending strength of 8300 g./mm.², and it was not broken when used for writing.

A graphite lead having a bending strength of 8000 g./mm.², which was not broken when used for writing, was also prepared by repeating the above procedures except that of 1800 g. of the epoxy resin, 700 g. was replaced by ethyl cellulose.

EXAMPLE 3

This Example illustrates the preparation of colored leads.

Red, blue and yellow colored leads were prepared in the same manner as in Example 1 except that the following three changes (1) to (3) were made to the preparation conditions:

(1) Starting materials

	Mixing ratio (on the weight basis)		
	Red	Blue	Yellow
5 Components:			
Epoxy resin (same as used in Example 1).....	9.0	9.0	11.0
Acrylonitrile/styrene copolymer (same as used in Example 1).....	8.0	8.0	8.0
Calcium stearate.....	15.0	15.0	14.0
10 Talc (average particle size=2.0 μ).....	60.0	60.0	60.0
Cromophthal Yellow A2R (Color index number=70600).....			7.0
Helio Fast Red BBN (Color index number=12370).....	8.0		
Heliogen Blue 6900 (Color index number=74160).....		8.0	

(2) Strands extrusion conditions

Cylinder temperature..... 145° C. (at the rear); 150° C. (at the front).
Die temperature..... 145° C.

(3) Lead-molding conditions

Cylinder temperature..... 130-140° C. (at the rear); 135-140° C. (at the center); 140-145° C. (at the front).
Die temperature..... 125-130° C.

25 Fine letters and lines could be written with use of each of the so prepared colored leads, and written letters and lines could be erased almost completely by an eraser. These colored leads had the following bending strength:

	G./mm. ²
30 Red Lead	5500
Blue Lead	5520
Yellow Lead	5350

What we claim is:

35 1. A slender, cylindrical pencil lead which consists essentially of a powdery coloring agent bonded by an uncured epoxy resin having an average molecular weight of from about 700 to about 7000 which is a reaction product of 2,2-bis(4'-hydroxyphenyl)propane with epichlorohydrin and which is solid at room temperature.

40 2. A slender, cylindrical pencil lead which consists essentially of a powdery coloring agent bonded by a mixture of at least 50% by weight of an uncured epoxy resin having an average molecular weight of from about 700 to 7000 which is a reaction product of 2,2-bis(4'-hydroxyphenyl)propane with epichlorohydrin and which is solid at room temperature and up to 50% by weight of a thermoplastic resin selected from acrylonitrile/styrene copolymer and ethyl cellulose.

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70 260-13 R, 41 C, 41R

- [54] PENCIL LEAD AND MANUFACTURING METHOD OF THE SAME
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- [51] Int. Cl.² C08K 3/04
- [58] Field of Search 106/19; 260/38; 264/211, 176

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- [57] ABSTRACT
- A pencil lead comprises an extrudate of a kneaded blend of a coloring material and a novolak resin or a derivative thereof.

7 Claims, No Drawings

PENCIL LEAD AND MANUFACTURING METHOD OF THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a pencil lead composition and also to an advantageous method for manufacturing such lead.

2. Description of the Prior Art

Pencil lead, for example, black lead, has heretofore been manufactured by blending a coloring material such as natural graphite or artificial graphite, with a clay binder, grinding the blend with water and kneading it, extruding the wet material so obtained into the appropriate form for a lead pencil, and after drying, baking it at elevated temperatures of about 1,000° C and further oil-immersing it. Such a method is complicated for a manufacturing process not only in that it involves a large number of steps but also because close control of the water content at the time of extrusion is required. Moreover, it is necessary to bake the flexible extrudate while maintaining it in a straight line. However, it is almost impossible to bake an endless length of lead continuously. Thus, there is an inherent limitation to the number and types of variations for such a manufacturing process.

In order to eliminate or improve upon these defects in the conventional pencil lead making process, various methods of obtaining lead without need for baking have been proposed. These methods use various kinds of thermoplastic or thermosetting synthetic resins as a binder and involve blending and kneading them with a colored material and extruding the blend through a screw type extruder. (For example, see Japanese Patent Publication Gazette Nos. 3363/1952, 2309/1967, 13368/1973, 18900/1973, 12300/1974 and 12302/1974, and Patent Public Disclosure Gazette Nos. 16214/1972 and 55017/1974.)

However, the leads obtained by these methods are significantly inferior in performance to conventional lead obtained by using clay as a binder and baking at elevated temperatures. Particularly, the H, F, HB and B classes of lead, which are in great demand, suffer from the defect that a finely shaved point is easily broken because these leads have insufficient strength.

Generally, the writing depth (or density) of lead and its strength are inversely related to one another; that is, the deeper the depth, the lower the strength. In lead blended with a resin as a binder, the strength increases directly with the amount of resin component but the depth decreases therewith. Although, in lead below 2H in depth, e.g., 3H, 4H, 5H, etc., there is no problem in practical applications with use of various synthetic resins, as described in the above-mentioned publications, the demand for pencil lead is mostly concentrated in the vicinity of the HB level. Therefore, if a lead of depth as high as HB cannot be made of high strength in a given process, the method suffers enormously from an industrial viewpoint. Consequently, it would be most desirable to have an approximately HB pencil lead of high strength which is fabricated using a synthetic resin binder.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a pencil lead having a depth of about HB level,

having satisfactorily high strength, and not requiring a baking step at elevated temperatures for its production.

This and other objects of this invention as will hereinafter become clear by the ensuing discussion have been attained by providing a pencil lead obtained by extruding a kneaded blend of a coloring material and novolak resin and/or a derivative thereof. The lead of the present invention can be particularly advantageously manufactured by blending a coloring material with novolak resin and/or a derivative thereof, kneading the blend so obtained and extruding it at a die temperature of 100° to 150° C and at an extruding pressure of from 200 to 3000 kg/cm².

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention various coloring materials can be used. For example, graphite is usually used for a black lead. The graphite used may be natural or artificial, and is desirably of a fine particle size. Scaly graphite is particularly preferred because it has good properties in the use of a brush. However, since such scaly graphite is expensive, soil graphite or artificial graphite may be appropriately mixed with it. Moreover, the graphite may be mixed with carbon black. In case of colored lead, the various conventional dyes and pigments can be used. Also, inorganic fillers such as talc, clay, calcium carbonate, and the like can be used as extenders.

A key feature of the present invention is the use of novolak resin and/or a derivative thereof alone or in combination with another ingredient. In general, a so-called phenol resin is a reaction product of a phenol, such as phenol, cresol or xylenol, with an aldehyde such as formaldehyde. It is well known that either a novolak resin or a resol resin may be obtained depending upon both the type of catalyst used in the reaction and the molar ratio of the aldehyde to the phenol. For example, in the reaction of phenol and formaldehyde, use of an acid catalyst, such as hydrochloric acid or oxalic acid, and a molar ratio of formaldehyde to phenol which is less than 1, generally produces a novolak resin. Use of an alkali catalyst, such as caustic soda, and a molar ratio of formaldehyde to phenol which is greater than 1 produces a resol resin. A resol resin sets upon heating to become a non-soluble and non-melting resin, while a novolak resin, which is thermoplastic, melts upon heating to become a sticky liquidlike substance and does not set. (However, the novolak resin does set when heated in the presence of formaldehyde, or hexamethylene-tetramine.) It is noted that the Patent Publication Gazette No. 27-3363/1952, on page 1, left column, lines 29 to 34, discloses that it is known to extrude the lead of a pencil by use of a pre-condensation product of a resin such as phenol formalin resin or urea formalin resin, as a binder and to set it by heat treatment at a relatively low temperature. Such a pre-condensation product of a phenol formalin resin obviously does not include the novolak resin used in the present invention since the prior art product is set by heating in the presence of no additives. The pencil lead prepared by thermosetting with a thermosetting phenol resin used as a binder not only possesses an inferior writing quality but also requires complicated manufacturing steps because of the necessary setting treatment after extruding.

The present invention makes use of a binder prepared from a novolak resin/or a derivative as men-

tioned above. Suitable derivatives of novolak resin include the novolak epoxy resin (epoxy novolak) prepared by reacting a novolak resin with epichlorohydrin in the presence of a caustic alkali, the etherified reaction product of a novolak resin with an alkyl halide in the presence of a caustic alkali, the reaction product of an epoxynovolak with an aryl halide and the like. The novolak resins and their derivatives to be used in the process of the present invention are preferably of a solidlike state and of high molecular weight greater than about 700. The process of the present invention makes use of said novolak resins or of their derivatives since they are thermoplastic without the combined use of a setting agent. Consequently, the novolak resins or their derivatives remain thermoplastic throughout the process. Therefore, all ingredients used in the process may be handled as thermoplastic substances in all steps of compounding, kneading and extruding. As a result, whenever inferior or non-standardized articles are obtained, the starting materials can be reused because all ingredients are thermoplastic.

In the process of the present invention, novolak resins and/or their derivatives can be used in combination with other thermoplastic resins. These other thermoplastic resins should preferably have an affinity for coloring agents, and the novolak resins and their derivatives. This affinity should include the ability of physical homogeneous mixing. Suitable other thermoplastic resins include, for example, styrene resins, vinyl chloride resins, vinyl acetate resins, and bisphenol epichlorohydrin derived epoxy resins, especially styrene resins such as polystyrene, and high impact polystyrene, as well as acrylonitrile-butadiene-styrene copolymer (ABS). Mixtures of these thermoplastic resins may also be used. Prior to the extruding step, lubricants, plasticizers, stabilizers, dispersion assistants and the like may be compounded with the ingredients. In particular, inclusion of a lubricant is preferred in order to improve the writing and extrusion qualities. Suitable lubricants include higher fatty acids (such as a fatty wax or stearic acid), metallic salts of a higher fatty acid (such as calcium stearate), waxes (such as paraffin wax) and amides (such as bis-stearyl amide of ethylene diamine).

The appropriate compounding ratio of ingredients in the process of the present invention varies with the kinds of materials used and the type of pencil lead desired with no strict general rule. However, a suitable composition for preparing a pencil lead of depth in the range of 2B -9H may be selected from the following range:

resin ingredient: 5-50% by weight, especially 5-30% by weight

coloring agent ingredient: 50-80% by weight

lubricant ingredient: 0-20% by weight, especially 5-15% by weight

Additionally, the optional thermoplastic resins mentioned above may be present in from 0-15% by weight, especially 2-15% by weight. In particular, a suitable composition for production of the highly desirable pencil lead of depth HB or thereabout may be selected from the following range:

resin ingredient: 15-20% by weight

coloring agent ingredient: 65-75% by weight

lubricant ingredient: 5-20% by weight

In compounding the ingredients in the process of preparing a pencil lead according to the present invention, the resin ingredient should preferably be previously atomized and should be blended while in the

powdered form. However, some resins, such as ABS, are difficult to atomize. In this case, blending may be performed by use of a conventional ribbon blender, a V-type blender or a Henschel mixer. Additionally, the ingredients of the present invention should preferably be fully kneaded before being extruded. In particular, when a great quantity of coloring agent is used, unsatisfactory kneading resulting in ensuing poor dispersion may cause the breaking of the pencil lead upon extrusion and unevenness in the quality of pencil lead produced. Preferred kneading devices include a mixing roll, a kneader, a Banbury, or a screw such as a multiple screw or a single screw. Regarding the single screw, because of the small bulk density of the material, it is necessary to choose one which easily effects intrusion. The kneading temperature is not critical and may be chosen according to the kinds of material and the compounding ratio employed. It usually is in the range of about 150° C - 170° C. A temperature higher than 170° C may cause the partial gelation of the novolak resin due to the pressure of the oxygen in the air. Any powder resulting from the kneading should be formed into a pellet by any adequate means.

Extrusion of the pencil lead of the present invention may be performed by use of a plunger type extruding machine or screw type extruding machine, preferably in a continuous production. The extruding temperature is preferred to be lower than 170° C in order to avoid gelation of the novolak resin. In particular, the temperature of the nozzle is preferred to be lower than 150° C. In general, a lower nozzle or die temperature and a high extruding pressure will yield a good pencil lead of great bending strength. Under these conditions, the lead material should be molded under high extruding pressure while sliding through the nozzle, overcoming the friction between the nozzle wall and itself. Therefore, an especially preferred extruding condition involves a temperature of 100° C to 150° C, preferably 110° to 140° C, and an extruding pressure (pressure at the nozzle inlet) of 200 to 3000 kg/cm² preferably 300 to 1000 kg/cm². The extruded lead material from the extruding machine is cooled by any adequate cooling means. Suitable means include water cooling during the lead's introduction into a guide roll, equipped with a water sprinkling facility, where it sets producing a pencil lead with no flexibility. It should be emphasized that continuous extrusion can produce continuously a pencil lead of infinite length.

The pencil lead prepared by the process of the present invention has a superior writing quality, far superior to that of the so-called clay lead prepared with a conventional clay binder. It eliminates the disadvantage of soiling the hand that touches the pencil lead. Furthermore, the pencil lead of this invention has a strength higher than that of a pencil lead prepared with other thermoplastic resins eliminating the disadvantages of the pointed end breaking. Additionally, it is to be stressed that the process for preparing a pencil lead according to the present invention involves steps simpler than those of the prior art process for preparing a clay lead. Moreover, it has the attendant advantages of an easily controlled operation, a good operational environment, the capability for easily and continuously producing a pencil lead of infinite length. Thus, it allows new concepts to be used in pencil lead manufacturing. In particular, if the pencil lead composition of the present invention is employed in the production of pencils having pencil rods of synthetic materials (such

as lowly expanded foamed synthetic resins), the continuous production of the pencil by combined extrusion of both the rod material and the lead material will be feasible.

Having generally described the invention, a more complete understanding can be obtained by reference to certain specific examples, which are included for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLE 1

A commercial novolak resin (average molecular weight of 900) was atomized in an atomizer. 18 parts by weight of the resulting novolak powder were added to 12 parts by weight of calcium stearate and 70 parts by weight of graphite (CSP made by Japan Graphite Company) and the mixture was blended by use of a Henschel mixer.

The resulting mixture was kneaded in a mixing roll at a roll temperature of 150°–160° C for 15 minutes. The ensuing sheet was roughly pulverized in the form of cubes of dimensions of 2–3 mm and used as the extruding material.

This material was extruded by use of an extruding machine having an aperture diameter of 3 mm and a die of diameter of 2.2 mm, under the extruding pressure of 400 Kg/cm², at the extruding rate of 3 Kg/hr, and at the temperatures described below. The resulting product was introduced to a guide roll and cooled by water.

temperature at cylinder 1 : 130° C.

temperature at cylinder 2 : 150° C.

temperature at the die : 120° C.

The resulting pencil lead had a softness of HB degree and a bending strength of 7,000 g/mm², far surpassing the bending strength of 5,000 g/mm² stipulated in JIS-S 6005. The pencil lead suffered from no problem of its pointed end breaking and had an excellent writing quality.

EXAMPLES 2–5

Pencil leads were prepared by extrusion as in Example 1, with varying composition ratios as shown in the following table where the properties of the resulting pencil leads are also shown.

	Example 2	Example 3	Example 4	Example 5	Control Example	
Composition ratio (wt.%)	Novolak resin	25	10	14	—	—
	Novolak-type epoxy resin	—	—	—	10	—
	ABS	—	10	6	10	20
	Calcium Stearate	10	10	10	10	15
	Graphite (CSP)	65	70	70	70	65
Properties of pencil lead	Softness (degree)	2H	HB	H	H	HB
	Bending Strength (g/mm ²)	8800	7600	9200	8300	5800
	Writing quality	Excellent	Excellent	Excellent	Excellent	Excellent
	Breakage of the pointed end	None	None	None	None	None

The novolak resins used were the same as that used in Example 1. Aralide ECN-1299 the tradename of an article made by Ciba Geigi Company (with a molecular weight of 1270) was used as the novolak-type epoxy resin. TFX-210 made by Mitsubishi Monsanto Chemical Company, was used as the ABS. Blending of the ABS was performed as follows. It was heated to a temperature in the vicinity of its softening point, wound around a roll, and kneaded while the powdered blends were slowly added to it.

As can be seen from the table, the pencil leads prepared in Examples 2–5 according to the present invention have excellent qualities. In particular, these pencil leads have a greater bending strength than that of the control Example where ABS alone was used as a binder, and did not suffer from breakage of their pointed ends.

Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

What is claimed as new and desired to be secured by letters patent of the United States is:

1. A pencil lead comprising an extrudate of a kneaded blend of a coloring material and a novolak resin or a novolak epoxy resin.

2. The pencil lead of claim 1 wherein the kneaded blend comprises (1) 50 to 80% by weight of a coloring material, (2) 5 to 50% by weight of said novolak or novolak epoxy resin and (3) 5 to 20% by weight of a lubricant ingredient.

3. The pencil lead of claim 2 wherein the kneaded blend additionally comprises 2 to 50% by weight of a thermoplastic resin selected from the group consisting of styrene resins, vinyl chloride resins, vinylacetate resins and bisphenol epichlorohydrine derived epoxy resin.

4. The pencil lead of claim 2 wherein the kneaded blend comprises (1) 50 to 80% by weight of a coloring material, (2) 5 to 30% by weight of said novolak or novolak epoxy resin, (3) 5 to 15% by weight of a lubricant ingredient and (4) 2 to 15% by weight of a thermoplastic resin selected from the group consisting of styrene resins, vinylchloride resins, vinylacetate resin and bisphenol epichlorohydrine derived epoxy resin.

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5. The pencil lead of claim 1 wherein said novolak or novolak epoxy resin is in the solid state.

6. The pencil lead of claim 1 wherein said coloring material is natural or artificial graphite.

7. A process for manufacturing a pencil lead charac-

terized by blending a coloring material with a novolak resin or derivative thereof and kneading, and extruding the resulting blend under a die temperature of 100° to 150° C and an extrusion pressure of 200 to 3,000 kg/cm².

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