

PATENT SPECIFICATION

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(54) A PENCIL HAVING A LEAD MADE OF A NEW COMPOSITION

(71) We, TEIJIN LIMITED, a Japanese body corporate, of No. 1, Umeda, Kita-Ku, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 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 a 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 this conventional method have the following two fatal defects.

30 (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 and diameter. 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.

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

45 The above defect (1) can readily be understood from the fact that in com-
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mercially 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 (which may be foamed). The reason is as follows:

55 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 substitution of a plastic material (which may be foamed) for such special wood in the art of the 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 thus no benefit is obtained by the substitution. 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 the plastic material by use of an apparatus resembling a die customarily used for coating electric wires. However, in order to make such a process practically workable, it is indispensable that leads should be continuous and have an endless length.

80 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. Patent 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 90

specification, the lead of No. 2½ grade (corresponding to grade F) has a bending strength of only 7300 psi (5110 g/mm²) and, from the viewpoint of the strength the lead proposed in the above specification cannot be a satisfactory practical substitute for the conventional product. Further, the specification of U. S. Patent 3,360,489 proposes the use as a binder of a polymer having a colloidal particle size, such as PVC latex. However, when polymer of the latex form is employed, though the firing step can be omitted, troublesome operations are necessary 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 satisfactory practical 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 colouring agents, it has been impossible to obtain pencil leads of sufficient practical quality as regards the hardness of grade H or HB.

Accordingly, it is a primary object of this invention to provide a pencil which can be made in endless lengths and which has a lead exhibiting satisfactory properties at a hardness of grade H or HB.

We have found that this object of this invention can be attained when the pencil lead is made of a composition which comprises a finely divided colouring agent dispersed in an uncured epoxy resin of the 2,2 - bis(4' - hydroxyphenyl)propane/epichlorohydrin type which is solid at room temperature and has an average molecular weight of from 700 to 7000, preferably from 1000 to 6000.

Since the epoxy resin binder is required to be uncured, the composition will generally not contain any substance capable of acting as a curing agent for the epoxy resin. Whereas in general the customary use of an epoxy resin is to form a three-dimensional cross-linked structure in the resin by curing it with a curing agent such as an amine or acid anhydride, in this invention the epoxy resin remains in the uncured, thermoplastic, state.

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 tradenames for products of Shell International Chemicals Corporation, Ciba Products Company and Dow Chemical Company, respectively; "Epikote" and "Araldite" are U.K. Registered Trade Marks.

All the powdery colouring 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 finely divided 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 specially 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 (% by weight)				
	Graphite powder	Epoxy Resin	Hardness Adjuster	
5	Graphite Lead of HB Hardness	70	12	18
10	Graphite Lead of H Hardness	70	18	12
	Graphite Lead of 4H Hardness	70	20.5	9.5
15	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 increase 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 in the starting material mixture.

In another embodiment of this invention pencils are provided with colored leads. In this embodiment, organic pigments are used as the finely divided 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 finely divided 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 such 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 mold-

ing 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 similar to that of the lead taught in the above-quoted specification of U. S. Patent No. 3,360,489. Therefore, it is not preferred to incorporate the additional 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 has 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/mm². 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/mm²), P stands for the minimum concentrated load (g) laid on the centre that can break the lead, L indicates the distance (mm) between the two supporting points (usually adjusted to 60 mm), and d designates the diameter of the lead.

Conventional endless graphite leads pre-

pared by employing plastics as binders have a bending strength of 3500 to 5000 g/mm², and the minimum bending strength passing the test standard stipulated by JIS is 5000 g/mm² 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 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 ("Tyril" [U.K. Registered Trade Mark] 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/cm².

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/mm². A lead having such a low bending strength has no great 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/mm², and it was not broken when used for writing.

- 5 A graphite lead having a bending strength of 8000 g/mm², 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.

10

This Example illustrate the preparation of colored leads.

Red, blue and yellow colored leads were prepared in the same manner as in Example 15 except that the following three changes (1) to (3) were made to the preparation conditions:

20 (1) Starting Materials Components

Mixing Ratio (on a weight basis)

25

Epoxy resin (same as used in Example 1)

Red Blue Yellow

9.0 9.0 11.0

30

Acrylonitrile/styrene copolymer (same as used in Example 1)

8.0 8.0 8.0

Calcium stearate

15.0 15.0 14.0

35

Talc (average particle size=2.0 μ)

60.0 60.0 60.0

Cromophthal Yellow A2R (Color Index Number=70600)

— — 7.0

40

Helio Fast Red BBN (Color Index Number=12370)

8.0 — —

Heliogen Blue 6900 (Color Index Number=74160)

— 8.0 —

45

(2) Strands Extrusion Conditions

Cylinder temperature

145°C. (at the rear)—
150°C. (at the front)

50

Die temperature

145°C.

(3) Lead-Molding Conditions

55

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.

60

- 65 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 strengths:

70 Red Lead 5500 g/mm²
Blue Lead 5520 g/mm²
Yellow Lead 5350 g/mm²

divided colouring agent dispersed in an uncured epoxy resin of the 2,2 - bis(4'-hydroxyphenyl)propane / epichlorohydrin type which is solid at room temperature and has a number average molecular weight of 700 to 7,000.

2. A pencil according to claim 1 wherein the epoxy resin has a number average molecular weight of 1,000 to 6,000.

3. A pencil according to claim 1 or 2 wherein the colouring agent is dispersed in a mixture of a said epoxy resin and another thermoplastic resin in amount up to 50% by weight of the resin mixture.

WHAT WE CLAIM IS:—

1. A pencil having a lead made of a composition which comprises a finely

The resulting graphite lead had a bending strength of 8300 g/mm², and it was not broken when used for writing.

A graphite lead having a bending strength of 8000 g/mm², 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.

10

This Example illustrate the preparation of colored leads.

Red, blue and yellow colored leads were prepared in the same manner as in Example 15 except that the following three changes (1) to (3) were made to the preparation conditions:

20 (1) Starting Materials Components

Mixing Ratio (on a weight basis)

25		Red	Blue	Yellow
	Epoxy resin (same as used in Example 1)	9.0	9.0	11.0
30	Acrylonitrile/styrene copolymer (same as used in Example 1)	8.0	8.0	8.0
	Calcium stearate	15.0	15.0	14.0
35	Talc (average particle size=2.0 μ)	60.0	60.0	60.0
	Cromophthal Yellow A2R (Color Index Number=70600)	—	—	7.0
40	Helio Fast Red BBN (Color Index Number=12370)	8.0	—	—
45	Heliogen Blue 6900 (Color Index Number=74160)	—	8.0	—

(2) Strands Extrusion Conditions

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

(3) Lead-Molding Conditions

55	Cylinder temperature	130—140°C (at the rear) 135—140°C. (at the center) 140—145°C. (at the front)
60	Die temperature	125—130°C.

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.

65 These colored leads had the following bending strengths:

70	Red Lead	5500 g/mm ²
	Blue Lead	5520 g/mm ²
	Yellow Lead	5350 g/mm ²

WHAT WE CLAIM IS:—

1. A pencil having a lead made of a composition which comprises a finely

divided colouring agent dispersed in an uncured epoxy resin of the 2,2 - bis(4'-hydroxyphenyl)propane / epichlorohydrin type which is solid at room temperature and has a number average molecular weight of 700 to 7,000.

2. A pencil according to claim 1 wherein the epoxy resin has a number average molecular weight of 1,000 to 6,000.

3. A pencil according to claim 1 or 2 wherein the colouring agent is dispersed in a mixture of a said epoxy resin and another thermoplastic resin in amount up to 50% by weight of the resin mixture.



4. A pencil according to claim 3 wherein the other thermoplastic resin is an acrylonitrile/styrene copolymer or ethyl cellulose.
5. A pencil according to any one of the preceding claims wherein the colouring agent is graphite.
6. A pencil according to any one of claims 1 to 4 wherein the colouring agent is an organic pigment and the composition also contains a white filler which imparts rigidity to the composition.
7. A pencil according to any one of the preceding claims which contains a metal soap to modify the hardness of the composition.
8. A pencil according to any one of the preceding claims having a casing of a synthetic polymer.
9. A pencil according to claim 1 substantially as described in any one of the foregoing examples.

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