July 26, 1966 D. L. RIPLEY 3,262,904

PENCIL LEADS

Filed Aug. 30, 1961

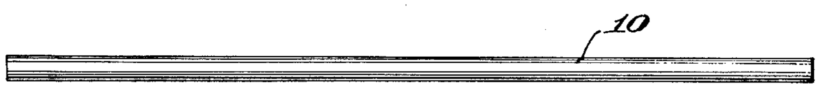

Fig. 1

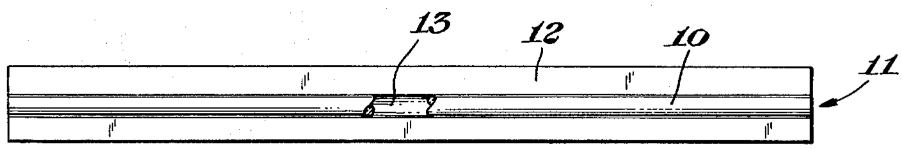

Fig. 2

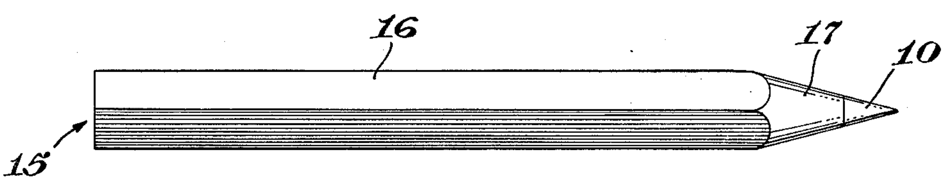

Fig. 3

INVENTOR.
Dennis L. Ripley
BY
Robert Bourgeois
AGENT

United States Patent Office

3,262,904

Patented July 26, 1966

3,262,904
PENCIL LEADS

Dennis L. Ripley, Bartlesville, Okla., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Filed Aug. 30, 1961, Ser. No. 135,067
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

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 $AR—CR{=}CH_2$, 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 $—CR{=}CH_2$ 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 ⅞ 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 considerable 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.

References Cited by the Examiner

UNITED STATES PATENTS

2,988,784 6/1961 Lorenian ---------- 120—83 XR

FOREIGN PATENTS

704,063 2/1954 Great Britain.

OTHER REFERENCES

Smith, "Vinyl Resins," Reinhold Plastics Application Series, Reinhold Pub. Corp., New York, 1958, page 72.

MORRIS LIEBMAN, *Primary Examiner.*

LAWRENCE CHARLES, *Examiner.*

R. R. RATH, K. B. CLARKE, J. S. WALDRON, *Assistant Examiners.*