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BITUMINOUS FLAME RESISTANT COMPOSITIONS AND ARTICLES COATED THEREWITH

John W. Olson, Hastings on Hudson, N. Y., and Charles W. Bechle, Sycamore, Ill., assignors to Anaconda Wire and Cable Company, a corporation of Delaware

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This invention relates to flame-resistant compositions, and is concerned particularly with the provision of a new synthetic organic flame-resistant composition having flame-resistant properties generally more uniform than and superior to the corresponding properties of heretofore known organic flame-resistant materials. The invention further contemplates articles of manufacture comprising a base structure having thereon a coating of the new flame-resistant composition.

Organic flame-resistant materials have long been used to reduce the inflammability of articles composed either wholly or in part of combustible organic substances. For example, electric wires insulated with rubber and surrounded by an organic fibrous jacket impregnated with asphaltic moisture-proofing compounds have been coated with flame-resistant composition to lessen the inflammability of the insulation and so to reduce the fire-hazard of the wiring installation. Similarly, it has been proposed to lessen the inflammability of roofing materials composed of a backing sheet and coated or impregnated with a moisture and weather-resistant material, such as asphalt or tar, by coating such roofing with a flame-resistant composition.

The flame-resistant material most commonly used heretofore has been stearin pitch. This material is the residue remaining in the stills after completion of the distillation of fatty materials, such as tallow. It is pitchy in character, usually black in color, and rather sticky even at ordinary temperatures, although its softening point is usually quite high. Upon heating to a temperature sufficiently above its softening point, it becomes fluid, and in this condition it may be applied in the form of a relatively thin coating to wire, roofing sheets, and other articles.

Stearin pitch as a flame-resistant material for use on wires, roofing materials, and the like possesses a number of drawbacks. In the first place, its flame-resistant properties are extremely variable, depending upon the particular type and grade of material from which it is produced and further depending upon the manner in which it is produced. At one extreme, some commercial stearin pitches are quite readily inflammable and are therefore valueless where flame resistance is a desired quality. At the other extreme, some commercial stearin pitches possess very good flame-resistant characteristics. Other grades of stearin pitch fall between these extremes in their flame-resistant properties. It is therefore difficult consistently to procure stearin pitch of uniformly good flame-resistance. In the second place, stearin pitch for flame-resistant uses is a relatively expensive commodity, and its price is subject to considerable fluctuation from time to time. In the third place, the natural stickiness of stearin pitch renders it unsatisfactory as a finishing coat on articles, such as wire or sheet roofing, which are coiled, rolled or stacked for shipping. Although generally such articles are best made flame-resistant by applying the stearin pitch as the final coating, this is not usually practicable because when the wire or roofing is coiled or rolled the stearin pitch causes the adjacent turns or layers to stick together.

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The present invention provides a new and improved flame-resistant composition which can be manufactured from readily available materials at a cost considerably less than the average price of stearin pitch; which can be manufactured with uniformly high flame-resistant properties; which may be made much less sticky than stearin pitch; and which with these advantages can be made even more flame-resistant than the best grades or stearin pitch heretofore available.

The new flame-resistant composition is of such character that it may be applied to the surface of an article and forms thereon a hard permanent coating. It is stable at temperatures incident to its normal use, but it is characterized by puffing and coking with the formation of an intumesced, difficultly combustible coky mass when exposed to flame. The composition comprises bitumen which imparts to the composition the property of forming a coky mass upon burning, to which bitumen has been added a substance which is characterized by puffing and becoming highly intumescent when exposed to flame, the added substance being a substantially neutral sulphated or phosphated acid petroleum sludge derivative. Compounds containing sulphated or phosphated derivatives of higher fatty acids, higher fatty acid esters, and higher fatty acid alcohols, characterized by puffing and becoming highly intumescent when exposed to flame, are described and claimed in our copending application Serial No. 415,145, filed October 15, 1941.

Bitumen is not highly flame-resistant and is incapable of imparting flame-resistance to articles to which it is applied. This probably is due to the fact that when bitumen is ignited on the surface of an inflammable article, any coky masses that may be formed are in such close contact with the inflammable article itself that combustion proceeds quite readily. However, when

an acid petroleum sludge derivative is added to the bitumen, and the resulting mixture is exposed to a flame, it puffs and forms a highly intumesced, difficultly combustible coky mass which is spaced from any underlying inflammable material. The coky mass thus is maintained out of close contact with readily inflammable material which would enable it to burn relatively easily, and at the same time the intumesced coky mass serves to insulate underlying inflammable material from the flame. Bitumens, and particularly asphaltic bitumens of at least moderately high softening points (upwards of 175° F.) have the property of burning with the formation of a coky mass and are especially satisfactory for the composition.

The acid petroleum sludge derivatives employed in the new composition are compounds containing sulphur-oxygen and phosphorus-oxygen radicals, such as sulphate, sulphone, and phosphate radicals, which are characterized by puffing and becoming highly intumescent when exposed to flame. These compounds by themselves are not especially flame-resistant, but in combination with bitumen form compositions having excellent flame-resisting properties.

Sulphated or phosphated petroleum hydrocarbons (either pure or in the form of mixtures) may be used successfully in preparing the new composition. Such sulphated or phosphated products may be produced by treatment of petroleum hydrocarbons with sulphuric or phosphoric acid. Especially economical commercial sources of mixtures of sulphated products of this character are the acid petroleum sludge resulting from sulphuric acid refining of petroleum, and the acid oil remaining after removal of tar from such acid sludges. These products are of complicated and uncertain composition, but they usually contain mono- and dialkyl sulphuric esters, sulphonates of aliphatic and aromatic compounds, and other compounds. These products may be used directly in preparing the new composition.

The sulphated and phosphated compounds prepared by treatment of petroleum oils with sulphuric or phosphoric acid are commonly acidic in reaction (unless purified). Compounds having an acid reaction are effective for producing flame-resistant compositions, but the presence of acid components is undesirable for many of the uses to which the new flame-resistant composition is adapted. Hence it is generally most satisfactory to employ neutralized (or naturally neutral) sulphated or phosphated compounds. In many cases such neutralized derivatives may be prepared by washing the acidic sulphated or phosphated compound to remove excess acid, and then, if necessary, treating with an alkaline agent such as sodium or ammonium hydroxide in sufficient amount to render the resulting product substantially neutral.

The flame-resistant composition is prepared by incorporating the acid petroleum sludge derivative in the bitumen. The bitumen may be heated to a temperature at which it becomes fluid and the acid sludge derivative may then be added and the mixture stirred to produce the composition. The bituminous composition so produced may be used directly to coat articles, or it may cut back with a suitable solvent or treated to produce an emulsion in any of the ways known in the art to produce thin liquid bituminous coating compounds.

Ordinarily the acid petroleum sludge derivative should be used in an amount equal to about 1% to 10% by weight of the composition, although larger amounts up to about 20% may in some cases prove desirable.

If desired, various modifying agents may be added to the composition to secure particular properties. For example, various oils, asphaltites, and mineral fillers may be added to the compositions. These are modifying agents well-known for imparting special properties to bitumens.

By way of example, a composition embodying the invention and comprising a bituminous vehicle and a sulphated product of petroleum hydrocarbons is described in detail below. It is understood, however, that the specific composition described below is not considered to limit the scope of the invention.

Any bitumen having the desired physical properties may be employed as the vehicle, but in order that the completed composition will form a sufficiently hard, non-sticky, flame-resistant coating on such articles as insulated wires and roofing elements, a bitumen having a softening point upwards of 175° F. should be employed. (The softening points referred to herein are determined by the A. S. T. M. standardized ring and ball method.) For most practical purposes a bitumen having a softening point from 210° F. to 250° F. is especially satisfactory. Bitumens of such relatively high softening points are desirable not only because they are sufficiently hard for most practical purposes, but also because in general such bitumens catch fire less readily than the softer bitumens of lower softening points. A bitumen which catches fire only with some difficulty is more suitable for use in making up the new flame-resistant composition than a bitumen which ignites readily.

Asphalts are particularly suitable bitumens for use in preparing the new composition. Any available asphalt may be employed, including natural asphalts, steam reduced asphalts, blown asphalts, and asphaltic residua (flux oils) of petroleum distillation. Especially satisfactory results have been obtained using an air blown flux oil having a softening point from 225° F. to 240° F. in preparing a flame-resistant composition for coating insulated wires.

Satisfactory flame-resistant compositions may be prepared by incorporating the sulphated (or phosphated) product in the bituminous substance, without any modifying agents being added. In many instances, however, it is desirable to employ other substances in the composition to modify its physical properties and to enhance its flame-resistance. Oily tempering agents which increase the weather-resistant qualities of the composition and make it less likely to crack in cold weather or to flow or run in hot weather are especially desirable. The oily tempering agent may be virtually any vegetable, animal or fish oil, or fatty acid derived therefrom. Drying oils are highly satisfactory for use as the oily tempering agent but semi-drying or non-drying oils have been used with success. Such oils in admixture with the bitumen, while lowering the softening point of the mixture, increase its weather-resisting properties and make it rather rubbery in quality, thus reducing its tendency to become brittle when cold, or fluid or semi-fluid when warmed to a moderately high temperature substantially below its softening point. Oils capable of thus modifying the properties of asphaltic materials

and similar bitumens are well known, and it is such oils that are embraced by the term "oily tempering agent."

The use of an oily tempering agent is desirable for the further reason that it can be made to increase the difficulty with which the bituminous vehicle is set afire, and hence to enhance the flame-resistance of the finished composition. Among the oily tempering agents which may be used with success may be mentioned fish oils, such as menhadin oil, pilchard oil, sardine oil, and herring oil; fish oil fatty acids; animal oils and fats, such as whale oil and beef tallow; and vegetable oils, such as soy bean oil, linseed oil, cottonseed oil, tung oil, coconut oil, peanut oil, etc. The oily tempering agent is added in suitable amount to the asphalt and other bitumen preferably while the latter is heated to a fluid condition. In general about 70% to 95% of the asphalt is employed in admixture with about 30% to 5 % of the oily tempering agent. Highly satisfactory results have been employed using mixtures composed of about 90% by weight of asphalt and about 10% weight of the oily tempering agent.

The oil serves as a flux for the asphalt, materially reducing its softening point. For many purposes this is undesirable, and accordingly it is generally best to blow the mixture of oil and asphalt with air at a sufficiently high temperature and for a sufficient period of time to increase the softening point to a satisfactorily high value, say from 210° F. to 250° F. Such blowing treatment may be carried out in conventional asphalt blowing equipment and in the manner usually employed for preparing blown asphalts. The temperature of the mixture during the blowing advantageously is about 450° F. to 600° F. It may in some cases be necessary to increase the temperature of the mixture while the blowing proceeds and as the softening point of the mixture increases. For example, blowing may be begun at about 450° F. and the temperature of the mixture may be increased as blowing proceeds to an ultimate value of about 600° F. In general, the softening point of the blown asphalt-oil mixture should be above 175° F., and preferably from about 210° F. to about 250° F., for use in preparing flame-resistant compositions suitable for coating wires, roofing elements and the like.

The blown mixture of asphalt or other bitumen and oil or other oily tempering agent is easier to handle in commercial operations than the asphalt alone, is more rubbery than the asphalt alone, and is less likely to crack in cold weather and less likely to run or flow at high outdoor temperatures. In addition it is less likely to bleed through paints applied over it on a wire or on a roofing element. It is, moreover, more difficult to ignite than the asphalt alone and so is a better vehicle for the flame-resistant composition.

It may be mentioned at this point that mixtures of an asphaltic bitumen and an oily tempering agent can, by blowing for a sufficient period of time, be made sufficiently flame-resistant so that when the blown mixture is applied to an insulated wire, the wire will pass the Underwriters' flame test. To accomplish this result, however, the mixture must be blown at a high temperature to an ultimate softening point of 300° F. or over. Blowing to such a high softening point is extremely hazardous, and the product obtained is markedly less flame-resistant than properly prepared compositions according to the invention made with blown oil-asphalt mixtures of lower softening point.

Various other modifying agents, in addition to or in place of the generally preferred oily tempering agent, may be employed. For example, mineral fillers, hardening agents such as gilsonite or other asphaltite, and other modifying agents may be mixed with the bituminous base.

The composition is completed by incorporating in the bituminous vehicle a sulphated (or phosphated) product of a petroleum hydrocarbon, which product is characterized by puffing and becoming highly intumescent when exposed to flame. Not all hydrocarbon sulphates or phosphates puff and become intumescent when exposed to flame, and compounds not possessing this property are not effective in the new composition. For example, tricresyl phosphate does not possess this property and so is not satisfactory for use in the composition. However, the necessary property of puffing and becoming intumescent when exposed to flame is characteristic of a great many sulphated and phosphated products of petroleum hydrocarbons, and all such compounds so characterized may be used with success. The suitability of any particular compound is readily ascertained by the simple test of exposing a small sample of the compound on a spatula to a flame, and observing whether or not it puffs and becomes intumescent.

Sulphated and phosphated derivatives of petroleum hydrocarbons suitable for use in the new composition commonly are prepared by treating a petroleum hydrocarbon with concentrated sulphuric or phosphoric acid. Substantially pure sulphated or phosphated derivatives may be employed, but it is generally more economical to employ commercially available reaction mixtures resulting from the treatment of petroleum products with sulphuric acid. Particularly economical sulphated petroleum derivatives suitable for use in the new composition are the acid petroleum sludge resulting from the treatment of petroleum products with sulphuric acid for refining purposes, and the acid oil resulting upon extraction of tar from such acid sludge. These materials are of complex composition but usually contain mono- and di-alkyl sulphuric esters, some alcohols, sulphonated aromatic compounds, oxidation and condensation products, and polymerization products.

Acid sludge and acid oil, and other sulphated and phosphated products resulting directly from treatment of petroleum products with sulphuric or phosphoric acid, are acidic. Although such compounds are effective for producing flame-resistant compositions, the presence of acid constitutents in compositions for coating such articles as wire and roofing elements is generally undesirable. Accordingly, it is preferred to employ neutralized sulphated or phosphated products in making up the flame-resistant composition.

Methods are known for neutralizing acid sludge and similar acidic materials by treating with water or steam to dissolve the acid and cause it to separate from the oily constituent. After separation of the water, which contains the bulk of the acid dissolved therein, the residual oily material may be treated with an alkaline material, such as sodium or ammonium hydroxide, to neutralize such acid as remains. Neutralized products of other acidic sulphated or

phosphated petroleum compounds may be prepared similarly.

Many neutralized sulphated (and phosphated) petroleum hydrocarbons are water-soluble. Water-soluble compounds generally are undesirable for use in the new composition, because many of the articles coated therewith must be exposed to the weather. Water-soluble constituents in a composition so exposed will eventually be washed away. Moreover, water-soluble sulphated or phosphated derivatives of the character herein described are in some cases capable of functioning as soaps, and are likely to cause the bitumen (or other vehicle of the composition) to emulsify and wash away. It is therefore preferred to employ water-insoluble neutralized sulphated or phosphated compounds in the composition.

Such water-insoluble compounds may be prepared by treating the water-soluble neutralized sulphated or phosphated derivative with the salt of a metal capable of precipitating an insoluble product. Salts of metals known to form substantially water-insoluble soaps, such, for example, as salts of calcium, copper, aluminum, lead, barium, etc., may be employed to precipitate such insoluble sulphated or phosphated products from neutralized acid sludge or the like. The water-insoluble product advantageously is precipitated by adding a water-soluble salt of the precipitating metal, as, for example, calcium chloride or copper sulphate, to the water-soluble material. The insoluble compound is precipitated and separates as a water-insoluble solid or viscous oily layer.

Water-insoluble neutralized sulphated or phosphated petroleum hydrocarbons also may be prepared by treating the slightly acidic sludge residue remaining after extraction of most of the acid from acid sludge with the hydroxide of the metal selected to form the insoluble compound. For example, this slightly acidic residue may be treated directly with calcium hydroxide to form a substantially neutralized water-insoluble sulphated petroleum hydrocarbon mixture which is well suited for use in the new composition.

The particular metal compound chosen to produce the insoluble neutralized sulphated or phosphated petroleum product is not critical. Calcium salts (or calcium hydroxide, depending upon the manner of forming the insoluble compound) are inexpensive and the calcium precipitated product is generally highly effective. In some cases it may be desirable to employ a compound of some other metal so as to impart particular properties to the insoluble product. The copper-precipitated product, for example, is somewhat toxic to fungus growths, and compositions prepared from such products are therefore especially suitable for use where resistance to deterioration from attack by fungi is important.

The sulphated (or phosphated) acid petroleum sludge derivative, preferably neutralized and water-insoluble, is readily incorporated in the bituminous vehicle while the latter is heated to a fluid condition. The sulphated derivative may be added to the fluid vehicle, and the mixture may be stirred or otherwise agitated to effect thorough admixture of the two components. The water-insoluble neutralized sulphated derivative of acid sludge is soluble in bituminous vehicles and is compatible therewith, so that no particular difficulty is experienced in mixing the two together. An amount of the sulphated (or phosphated) product from 1% to 10% (or more if desired) by weight of the composition is generally effective for producing a highly flame-resistant composition. A small amount within this range is effective if the bituminous base itself possesses moderate flame-resistance, whereas a relatively large amount within the stated range is desirable if the base itself is fairly readily ignited. For most purposes, using an asphalt-oil base blown to a softening point of 210° F. to 250° F., about 3% to 5% by weight of the sulphated product results in a composition having excellent flame-resistance.

The new composition may be applied to articles in much the same manner in which stearin pitch has heretofore been applied. For example, the composition may be applied to an insulated wire by drawing the wire through a molten bath of the composition, and thence through a wiping die to remove excess composition. It may be applied to roofing sheets or other roofing elements by brushing the molten composition on to the surface of the sheet, or by other methods commonly emplyed for coating roofing elements with bituminous materials or with stearin pitch.

The new composition may readily be made sufficiently flame-resistant so that a rubber-insulated, fabric-covered wire coated therewith easily passes the Underwriters' flame test. In this connection it may be noted that neither the vehicle of the new composition nor the sulphated or phosphated compound are by themselves particularly flame-resistant, and neither, when coated on a rubber-insulated wire, will by itself enable the wire to pass the flame test. Bituminous vehicles of the character herein specifically described burn quite readily, and the same is generally true of the sulphated or phosphated products of petroleum hydrocarbons. The latter, however, puff and become highly intumescent in the flame, and in consequence of this property the vehicle in which it is incorporated is caused to puff and form an intumescent, difficulty combustible coky mass which is spaced from underlying inflammable material and so protects it from ignition by a flame.

The new flame-resistant composition can be made so as to be much less sticky than stearin pitch by employing a non-sticky bituminous (or other) vehicle. A bituminous vehicle prepared from asphalt and an animal, fish or vegetable oil is, generally speaking, much less sticky than stearin pitch, and the composition prepared from such a base is correspondingly much less sticky. An advantage of the use of asphaltic residum (flux oil) as the asphaltic component of the vehicle is that, when blown with a suitable oil to a high enough softening point, it yields a base having no appreciable stickiness or tackiness at ordinary temperatures.

The new composition can be made considerably more flame-resistant than even the best grades of stearin pitch, and successive batches of the new composition can be prepared with uniformly high flame-resistant properties. Because of the excellent flame-resistant qualities of compositions prepared according to the invention, it is possible to apply such compositions to insulated wire beneath relatively inflammable coatings of asphalt or wax without destroying the flame-resistance imparted to the wire by the new composition. For example, stearin pitch has heretofore been applied to wires to render them flame-resistant by first saturating the fibrous jacket on the wire with an asphaltic compound, and applying the stearin pitch over the asphalt im-

pregnated jacket. Frequently a thin wax coating is applied over the stearin pitch, but where flame-resistance is desired the asphaltic constituents are always applied under the stearin pitch. The new composition may be employed to saturate the fibrous jacket, and asphaltic or wax (or both) finishing coats may be applied thereover.

The new composition can be made highly resistant to moisture penetration by the selection of an appropriate vehicle. For example, compositions made with a bituminous base are substantially as moisture-resistant as the straight bituminous vehicle. Hence such compositions may be employed to replace the asphaltic moisture-resistant saturate commonly applied to wires and roofing compounds, without thereby sacrificing protection of the wire or roofing from moisture penetration, but with the attainment of a considerable increase in protection against fire hazard.

The new composition is prepared from relatively inexpensive materials, and in its preferred form may be made more inexpensively than it is possible to procure stearin pitch.

We claim:

1. A bituminous flame-resistant composition capable of being applied to the surface of an article and of forming thereon a hard permanent coating which is stable at temperatures incident to its normal use and is further characterized by puffing and coking with the formation of an intumesced difficultly combustible coky mass when exposed to flame, said composition being in the form of an intimate mixture consisting essentially of a bitumen having a softening point upwards of 175° F., to which has been added a substantially neutral, water-insoluble sulphated acid petroleum sludge derivative characterized by puffing and becoming highly intumescent when exposed to flame.

2. A bituminous flame-resistant composition capable of being applied to the surface of an article and of forming thereon a hard permanent coating which is stable at temperatures incident to its normal use and is further characterized by puffing and coking with the formation of an intumesced difficultly combustible coky mass when exposed to flame, said composition being in the form of an intimate mixture consisting essentially of a bitumen having a softening point upwards of 175° F., to which has been added a substantially neutral water-insoluble acid petroleum sludge derivative selected from the group consisting of sulphated and phosphated sludge derivatives characterized by puffing and becoming highly intumescent when exposed to flame.

3. A bituminous flame-resistant composition capable of being applied to the surface of an article and of forming thereon a hard permanent coating which is stable at temperatures incident to its normal use and is further characterized by puffing and coking with the formation of an intumesced difficultly combustible coky mass when exposed to flame, said composition being in the form of an intimate mixture consisting essentially of a bitumen having a softening point upwards of 175° F., and a substantially neutral, water-insoluble acid petroleum sludge derivative selected from the group consisting of sulphated and phosphated sludge derivatives characterized by puffing and becoming highly intumescent when exposed to flame, said composition having a softening point upwards of 175° F.

4. A bituminous flame-resistant composition

capable of being applied to the surface of an article and of forming thereon a hard permanent coating which is stable at temperatures incident to its normal use and is further characterized by puffing and coking with the formation of an intumesced difficultly combustible coky mass when exposed to flame, said composition being in the form of an intimate mixture consisting essentially of a bitumen having a softening point upwards of 175° F., to which has been added a phosphated acid petroleum sludge derivative characterized by puffing and becoming highly intumescent when exposed to flame.

5. An article of manufacture comprising a base structure having thereon a coating of a bituminous flame-resistant composition which is stable at temperatures to which the article is normally subjected and which is characterized by puffing and coking with the formation of an intumesced difficultly combustible coky mass when exposed to flame, said composition being in the form of an intimate mixture consisting essentially of a bitumen having a softening point upwards of 175° F., to which has been added a substantially neutral water-insoluble acid petroleum sludge derivative selected from the group consisting of sulphated and phosphated sludge derivatives characterized by puffing and becoming highly intumescent when exposed to flame.

6. An article of manufacture comprising a base structure having thereon a coating of a bituminous flame-resistant composition which is stable at temperatures to which the article is normally subjected and which is characterized by puffing and coking with the formation of an intumesced difficultly combustible coky mass when exposed to flame, said composition being in the form of an intimate mixture consisting essentially of a bitumen having a softening point upwards of 175° F., to which has been added a substantially neutral water-insoluble sulphated acid petroleum sludge derivative characterized by puffing and becoming highly intumescent when exposed to flame.

7. An article of manufacture comprising a base structure having thereon a coating of a bituminous flame-resistant composition which is stable at temperatures to which the article is normally subjected and which is characterized by puffing and coking with the formation of an intumesced difficultly combustible coky mass when exposed to flame, said composition being in the form of an intimate mixture consisting essentially of a bitumen having a softening point upwards of 175° F., to which has been added a substantially neutral water-insoluble phosphated acid petroleum sludge derivative characterized by puffing and becoming highly intumescent when exposed to flame.

JOHN W. OLSON.
CHARLES W. BECHLE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,339,853	Hemmer	Jan. 25, 1944
2,305,324	Snyder	Dec. 15, 1942
2,299,469	D'Antal	Oct. 20, 1942
2,071,354	Morgan	Feb. 23, 1937
1,888,295	Smith	Nov. 22, 1932

(Other references on following page)

Number	Name	Date
1,872,358	Styer	Aug. 16, 1932
1,856,756	Frigiola	May 3, 1932
1,842,857	Bolgar	Jan. 26, 1932
1,834,552	Sadtler et al.	Dec. 1, 1931
1,720,487	Lichtenstein	July 9, 1929
1,663,577	Watson	Mar. 27, 1928
1,444,051	Allison	Feb. 6, 1923
1,231,985	Baskerville	July 3, 1917
1,167,195	Matter	Jan. 4, 1916

FOREIGN PATENTS

Number	Country	Date
519,119	Great Britain	Mar. 18, 1940
188,354	Great Britain	Nov. 6, 1922

OTHER REFERENCES

Abraham, Asphalts and Allied Substances, 4th ed. 1938, pages 45, 628, 720–723.