

Patented June 1, 1948

2,442,707

UNITED STATES PATENT OFFICE

2,442,707

BITUMINOUS FLAME RESISTANT COMPOSITIONS AND ARTICLES COATED THEREWITH

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No Drawing. Application October 15, 1941,
Serial No. 415,145

11 Claims. (Cl. 117-128)

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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 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 aliphatic moisture-proofing compounds have been coated with flame-resistant compositions to lessen the inflammability of the insulation and so 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. As the other extreme, some commercial stearin pitches possess very good flame-resistant characteristics. Other grades of stearin pitch fall between these extreme in their flame-resistant properties. It is therefore difficult consistently to procure stearin pitch of uniformly good flame-resistance. In the second

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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.

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 of stearin pitch heretofore available.

The new flame-resistant composition of the present invention 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 is characterized by puffing and coking with the formation of an intumescent, 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 selected from the group consisting of sulphated and phosphated derivatives of a substance of the group consisting of higher fatty acids, higher fatty acid esters, and higher fatty acid alcohols, the sulphated or phosphated derivative being characterized by puffing and becoming highly intumescent when exposed to flame. Compounds containing sulphated or phosphated petroleum sludge derivatives as substances characterized by puffing and becoming highly intumescent when exposed to flame are described and claimed in our copending application Serial No. 415,144, 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 organic sulphated or an organic phosphated derivative of the character specified is added to the bitumen, and the resulting mixture is exposed to a flame, it puffs and forms a highly intumescent, 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 intumescent 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.) are especially satisfactory vehicles for the composition.

Especially satisfactory vehicles for the new flame-resistant compositions are composed of a bitumen of relatively high softening point in admixture with an oily tempering agent. 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 sulphated and phosphated derivatives employed in the new composition are those derivatives of higher fatty acids, higher fatty acid esters, and higher fatty acid alcohols containing sulphur-oxygen or 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. A very large number of sulphated and phosphated derivatives of fatty acids, fatty acid esters and fatty acid alcohols possess the requisite property of puffing and becoming intumescent when exposed to flame. Whether or not any particular compound possesses this property is readily ascertained by the simple test of exposing a small sample on a spatula to a flame, and observing whether or not it puffs and becomes intumescent.

The sulphated or phosphated derivatives employed in the new composition generally are prepared by treating fatty acids, fatty acid esters, or fatty acid alcohols with sulphuric or phosphoric acid (or equivalent sulphating or phosphating agent). The most readily available derivatives of this class are those prepared by treating fatty acid oils, especially animal, fish or vegetable oils containing fatty acid glycerides, with concentrated sulphuric acid, or less commonly with concentrated phosphoric acid. Such treatment results in a complex reaction mixture usually containing, among other substances, a proportion of organic sulphates (or phosphates), lactones, various types of esters, and some polymerization products. The particular composition of the reaction mixture is immaterial to the

invention, however, for in general sulphated or phosphated derivatives of fatty acids, fatty acid esters, and fatty acid alcohols, and particularly such derivatives of fatty acid oils (especially animal, fish or vegetable oils), may be used with success in preparing the new composition.

The sulphated or phosphated derivatives prepared merely by treatment of fatty acid oils (or other fatty acid material or compound) are acidic in reaction. Derivatives having an acid reaction are undesirable for many of the uses to which the new composition is adapted, and accordingly it is preferred to employ neutralized sulphated or phosphated derivatives. Such neutralized derivatives generally are prepared by first washing with an aqueous salt solution (e. g., sodium chloride or sodium sulphate solution) the reaction product resulting from treatment of the oil or other substance with sulphuric or phosphoric acid, and then treating the washed reaction product with an alkaline agent, such as sodium or ammonium hydroxide, in sufficient amount to render the product substantially neutral.

The sulphated and phosphated derivatives which have been neutralized with the common neutralizing agents such as sodium hydroxide or ammonium hydroxide are water-soluble. This property renders the material unsuitable for uses involving exposure to moisture, as, for example, exposure to the weather. It is therefore preferred to employ water-insoluble neutralized sulphated or phosphated derivatives of the character referred to above. Such derivatives may be prepared by treating the sulphated product, after neutralization with sodium hydroxide or other neutralizing agent yielding a water-soluble product, with a salt of a metal capable of forming an insoluble derivative. Calcium salts, copper salts, aluminum salts, barium salts, and lead salts are representative of the metal salts capable of forming water-insoluble sulphated or phosphated derivatives. Such insoluble derivatives also may be prepared by neutralizing the acid-treated fatty acid oil or other fatty acid material, after washing, with the hydroxide of a metal capable of precipitating a substantially water-insoluble derivative. For example, calcium hydroxide may be so employed.

Although it is possible to employ with success the sulphated or phosphated derivatives of fatty acids, fatty acid esters, and fatty acid alcohols generally, it is preferred to employ sulphated or phosphated derivatives, and particularly sulphated derivatives, of fatty acid oils. By the term "fatty acid oils" we mean those oils, either natural or synthetic, composed largely of free fatty acids or fatty acid alcohols or esters (such as fatty acid glycerides), and especially we mean natural animal, fish or vegetable oils rich in such fatty acid constituents. Derivatives prepared from fatty acid oils, especially the sulphated derivatives, are preferred because they are readily available, comparatively inexpensive, and in general yield compositions according to the invention which have exceptionally high flame-resistant properties.

The sulphated or phosphated product should be resistant to thermal decomposition at the temperatures to which it must be heated in preparing the composition and applying it to articles. For this purpose the sulphated or phosphated product ordinarily should be resistant to thermal decomposition at elevated temperatures up to at least 300° F. Sulphated and phosphated deriva-

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tives of fatty acids, fatty acid esters, and fatty acid alcohols of the character employed in the new composition generally are resistant to thermal decomposition at temperatures as high as 300° F. to 500° F.

The flame resistant composition is prepared by incorporating the sulphated or phosphated derivative in the bitumen. This may be done in various ways; e. g., the bitumen may be heated to a temperature at which it becomes fluid, and the phosphated or sulphated 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 be 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.

The sulphated or phosphated derivative may dissolve in the bitumen, or it may be finely dispersed therein, and in either case an effective flame-resistant composition is produced. Generally, however, the sulphated and phosphated derivatives of fatty acids, fatty acid esters, and fatty acid alcohols are soluble in and otherwise thoroughly compatible with the bitumen.

Ordinarily the sulphated or phosphated compound 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.

The new composition may be employed in the manufacture of articles which it is desired to provide with a flame-resistant coating. The article of manufacture comprises a base structure having thereon a coating of the herein-described flame-resistant composition. A particularly useful article comprises an insulated wire comprising a metallic conductor, insulating material applied to the conductor, and on said insulating material a coating of the flame-resistant composition herein-described. Another particularly useful article in accordance with the invention comprises a roofing material comprising a backing sheet having thereon a coating of a flame-resistant composition of the character herein-described.

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.

Inasmuch as the new composition is intended primarily for use as a flame-resistant coating on articles such 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

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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 derivative of a fatty acid, a fatty acid ester, or a fatty acid alcohol 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. These oily tempering agents are desirable for the further reason that they can be made to increase the difficulty with which the bituminous base is set afire, and hence to enhance the flame-resistance of the finished composition. Vegetable, animal, and fish oils are well known to be excellent fluxes for asphalts and to increase their weather-resistant properties, and such materials constitute the class of oily tempering agents advantageously employed in the composition.

The oily tempering agent may be drying, semi-drying, or non-drying. Among the oily tempering agents which have been used with success may be mentioned fish oils, such as menhaden 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, cotton-seed 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% by weight of the oil or other 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 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 base 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 the sulphated or phosphated derivative of a fatty acid, a fatty acid ester, or a fatty acid alcohol in the bituminous base. Any such sulphated derivative may be employed in preparing the composition, but in general it is preferred to employ a sulphated or phosphated derivative of a fatty acid oil, especially a natural animal, vegetable or fish oil. Such oils are composed largely of various fatty acid glycerides.

The sulphated product may be prepared by treating the oil (or other fatty acid, fatty acid ester, or fatty acid alcohol) with concentrated sulphuric or phosphoric acid. The resulting sulphated product generally is a complex mixture of a number of substances, usually including a proportion of organic sulphates, lactones, esters, and polymerization products. Sulphated derivatives of castor oil are highly satisfactory, and since they are manufactured in large quantities to produce Turkey-red oil for the textile industry, they are readily available. Sulphated or phosphated derivatives of other oils or fatty acid compounds are also effective. For example, sulphated or phosphated derivatives of olive oil, soy bean oil, rape oil, cottonseed oil, peanut oil, coconut oil, palm oil, palm kernel oil, beef tallow, menhaden oil, pilchard oil, oleic acid (red oil), etc., may be employed in place of the sulphated or phosphated derivative of castor oil.

Some oils from among those mentioned above contain a higher percentage of unsaturated compounds than others, and such oils are better adapted to the production of effective sulphated or phosphated products than are the oils con-

taining very high proportions of saturated constituents. Castor oil is composed largely of the glyceride of ricinoleic acid, an unsaturated compound, and is well adapted for the preparation of sulphated or phosphated derivatives for use in the new composition. Since sulphated castor oil is extensively manufactured, it is a readily available material for use in preparing the new composition and has been found to be highly effective.

Sulphated castor oil and other sulphated and phosphated derivatives resulting directly from treatment of the oil or other fatty acid substance with sulphuric or phosphoric acid are acidic. The presence of acid constituents in compositions for coating such articles as wire and roofing elements is generally undesirable, and accordingly it is preferred to employ a neutralized sulphated or phosphated derivative in making up the flame-resistant composition. Neutralized sulphated castor oil is prepared by first washing the castor oil-sulphuric acid reaction mixture with a solution of sodium chloride or sodium sulphate to remove excess acid, and then treating with an alkaline agent, such as sodium or ammonium hydroxide. Neutralized products of other sulphated or phosphated derivatives may be prepared similarly.

Neutralized sulphated castor oil prepared in the manner just described (using sodium or ammonium hydroxide) is water-soluble. The same is true in general of other sulphated or phosphated derivatives neutralized with an alkali metal or ammonia caustic. Water-soluble compounds generally are undesirable for use in the new flame-resistant composition, because many of the articles coated with the composition 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 employed are in many instances capable of functioning as soaps, and are likely to cause the asphalt or other bituminous constituent of the composition to emulsify and wash away. Consequently, it is preferred to employ water-insoluble neutralized sulphated or phosphated derivatives in the new composition.

Such water-insoluble materials 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 practically any of the 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 the corresponding water-insoluble sulphated or phosphated product. In preparing the water-insoluble product in this manner, it is preferable to employ a soluble salt of the chosen metal, as, for example, calcium chloride or copper sulphate. It is desirable also to add the metal salt precipitant to the soluble neutralized sulphated or phosphated product while the latter is at an elevated temperature, preferably approaching its boiling point, as in this manner the precipitate develops in a form which is fairly easily separated from the residual liquor.

Water-insoluble neutralized sulphated or phosphated derivatives also may be prepared by treating the sulphated or phosphated product, after washing to remove excess acid but before neutralizing directly with the hydroxide of the metal selected to form the insoluble material. For ex-

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ample, the washed acidic sulphated or phosphated product may be treated directly with calcium hydroxide to form a substantially neutralized water-insoluble sulphated or phosphated product eminently suitable for use in the new composition.

The particular metal compound chosen to produce the insoluble neutralized sulphated or phosphated 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 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 toxic to fungus growths, and compositions prepared from such products are therefore especially suitable for use where resistance to deterioration from fungus growth is important.

The sulphated or phosphated product, preferably neutralized and water-insoluble, is readily incorporated in the bituminous base of the composition while the latter is heated to a fluid condition. The sulphated or phosphated derivative may be added to the fluid bitumen, and the mixture may be stirred or otherwise agitated to effect thorough admixture of the two components. Sulphated and phosphated derivatives of the character herein-described generally are soluble in and compatible with bituminous vehicles, so that no particular difficulty is experienced in mixing the two together. An amount of the sulphated or phosphated product from 1% to 10% 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 employed for coating roofing elements with bituminous materials or with stearin pitch.

The following specific examples illustrate the preparation of a flame-resistant composition in accordance with the invention:

Example A.—An air-blown asphalt having a softening point of about 140° F. was heated to a fluid condition and mixed with menhaden oil in the proportions of about 90% asphalt and 10% oil. The resulting mixture was blown with air at a temperature of about 500° F. until its softening point had been raised to between 225° F. and 240° F., with a penetration of about 8 to 10. A water-insoluble neutralized product of sulphated castor oil was prepared by treating commercial Turkey red oil, heated to a temperature approaching its boiling point, with calcium chloride, and separating the resulting precipitate from the

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residual liquor. The precipitate thus obtained was incorporated by stirring into the air-blown asphalt-fish oil base while the latter was heated to a fluid condition. About 5% of the insoluble neutralized sulphated product, by weight of the composition, was employed. The resulting composition was applied to an insulated wire having an insulation of rubber surrounded by an asphalt-impregnated cotton braid by drawing the wire through a molten mass of the composition, and thence through a wiping die to remove excess composition. Upon cooling the wire, the coating was found to be continuous, adhering, and considerably less tacky or sticky than a similarly applied coating of stearin pitch. The wire was subjected to the standard underwriters' flame test and passed readily. A wire coated in a similar manner but with the asphalt-fish oil base not containing the sulphated product, failed to pass the underwriters' flame test.

Example B.—An asphaltic residuum (flux oil) having a ball and ring softening point of about 80° F. was heated to a fluid condition and mixed with coconut oil in the proportions of about 90% asphaltic residuum and about 10% by weight of the oil. The resulting mixture was blown with air until its softening point was increased to about 225° F. to 240° F. A water-insoluble neutralized sulphated derivative of castor oil was prepared by treating commercial Turkey red oil at a temperature approaching its boiling point with copper sulphate, and separating the resulting precipitate from the residual liquor. The precipitate thus obtained was incorporated in the blown asphaltic base while the latter was heated to a fluid temperature, in the proportions of about 5% by weight of the insoluble sulphated product, to 95% of the bituminous base. The composition thus prepared was applied to a wire having a rubber insulation surrounded by an asphalt-impregnated cotton braid by drawing the wire through a molten mass of the composition and thence through a wiping die. The thus-coated wire, upon cooling, was found to have a smooth, non-tacky and non-sticky surface resembling patent leather in appearance and feel. The wire was subjected to the underwriters' flame test and passed easily. A wire coated with the blown asphaltic-residuum-coconut-oil base to which no sulphated or phosphated derivative has been added failed to pass the underwriters' flame test, although the asphalt alone burned with some coke formation.

It is evident from the foregoing examples that the new composition may readily be made sufficiently flame-resistant so that a rubber-insulated, fabric-covered wire coated therewith easily passes the rigid underwriters' flame test. In this connection it may be noted that neither the vehicle of the new composition nor the sulphated or phosphated derivative 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. The sulphated or phosphated derivative, however, puffs and becomes 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, difficultly 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 or base 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 residuum (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 impregnated 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 is substantially as moisture-resistant as the straight bituminous vehicle. Hence such compositions may be employed to replace the asphaltic moisture-resistant saturants 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 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 water-insoluble substance selected from the group consisting of sulphated and phosphated derivatives of a substance of the group consisting of higher fatty acids, higher fatty acid esters, and higher fatty acid alcohols, the sulphated or phosphated derivative being 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 sulphated fatty acid oil derivative 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., an oily tempering agent of the group consisting of animal and vegetable oils, and a substantially neutral, water-insoluble sulphated fatty acid oil derivative 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 substantially neutral, water-insoluble acid sulphated castor oil derivative characterized by puffing and becoming highly intumescent when exposed to flame.

5. A bituminous flame-resistant composition consisting essentially of a bitumen having a softening point upwards of 175° F. in admixture with a water-insoluble sulphated calcium derivative of fish oil.

6. 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 fatty acid oil derivative characterized by puffing and becoming highly intumescent when exposed to flame.

7. A flame-resistant insulated wire comprising a metallic conductor, insulating material applied to said conductor, and on said insulating material a coating of a bituminous flame-resistant composition which is stable at temperatures to which the wire 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., and a substance of the group consisting of sulphated and phosphated derivatives of a substance of the group consisting of higher fatty acids, higher fatty acid

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esters, and higher fatty acid alcohols, the sulphated or phosphated derivative being characterized by puffing and becoming highly intumescent when exposed to flame.

8. A flame-resistant insulated wire comprising a metallic conductor, insulating material applied to said conductor, and on said insulating material a coating of a bituminous flame-resistant composition which is stable at temperatures to which the wire 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. and a substantially neutral, water-insoluble substance of the group consisting of sulphated and phosphated derivatives of a substance of the group consisting of higher fatty acids, higher fatty acid esters, and higher fatty acid alcohols, the sulphated or phosphated derivative being characterized by puffing and becoming highly intumescent when exposed to flame.

9. A flame-resistant insulated wire comprising a metallic conductor, insulating material applied to said conductor, and on said insulating material a coating of a bituminous flame-resistant composition which is stable at temperatures to which the wire normally is 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 fatty acid oil derivative characterized by puffing and becoming highly intumescent when exposed to flame.

10. A flame-resistant insulated wire comprising a metallic conductor, insulating material applied to said conductor, and on said insulating material a coating of a bituminous flame-resistant composition which is stable at temperatures to which the wire normally is 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 an asphaltic bitumen having a softening point upwards of 175° F., an oily tempering agent of the group consisting of animal and vegetable oils, and a substantially neutral, water-insoluble sulphated fatty

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acid oil derivative characterized by puffing and becoming highly intumescent when exposed to flame.

11. A flame-resistant roofing material comprising a backing sheet having thereon a coating of a bituminous flame-resistant composition which is stable at temperatures to which the roofing normally is 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 substance of the group consisting of sulphated and phosphated derivatives of a substance of the group consisting of higher fatty acids, higher fatty acid esters, and higher fatty acid alcohols, the sulphated or phosphated derivative being characterized by puffing and becoming highly intumescent when exposed to flame.

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Certificate of Correction

Patent No. 2,442,707.

June 1, 1948.

JOHN W. OLSON ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 1, line 17, for "alphaltic" read *asphaltic*; line 49, for "As the" read *At the*; column 10, line 51, for "has been" read *had been*; column 14, line 39, list of references cited, for "Fugiola" read *Frigiola*; line 42, for "Lichtenstein" read *Lichtenstern*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of September, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.