Patented Aug. 14, 1945

2,382,337

UNITED STATES PATENT OFFICE

2,382,337

BITUMINOUS PROTECTIVE COMPOSITIONS

Harold Schiller, Los Angeles, Calif., assignor to Socony-Vacuum Oil Company, Incorporated, New York, N. Y., a corporation of New York

No Drawing. Application June 1, 1943, Serial No. 489,298

4 Claims. (Cl. 106—18)

The object of the invention is to provide a novel and effective method for protecting articles made of vegetable fibre—nets, rope, twine, thread, lines and loosely woven fabrics—from the combined effects of bacterial rotting, abrasion and exposure to sunlight.

It is old practice to saturate fishing nets and similar articles with hot wood tar or coal tar. This treatment is effective in increasing the resistance to wear and to the effects of sunlight but has relatively little bactericidal effect. It is undesirable as greatly increasing the weight of the article, often by as much as 100 percent, and in making it stiff and difficult to handle.

Such tars have also been used in the form of solutions in volatile solvents, with much the same final results and with added cost and hazard incident to the evaporation of expensive and usually inflammable solvents.

Another treatment which has been proposed and which is effective against bacterial action is to saturate the net or other fibrous article with a solution of copper soap in naphtha or in dilute ammonia. This treatment offers very little protection against wear or the deleterious effects of the ultra-violet constituent of sunlight and the copper soap films deteriorate rapidly on contact with sea water.

I propose to combine and greatly to facilitate the application of these two treatments and at the same time materially to prolong the useful life of the bactericide, by immersing the nets or other articles in an aqueous emulsion having tar or asphalt as the dispersed phase and a soap of a bactericidal metal in either the dispersed or the continuous phase according to the manner in which the treating liquid is prepared.

The bituminous constituent of the treating liquid may be a reduced wood tar or coal tar or a soft asphalt. An asphalt produced by the steam reduction of Pacific Coast or Gulf Coast petroleum to a penetration ranging from 75 to 100 at 77° F. is preferred for most purposes. Asphalts which are too hard reduce the pliability of the treated article while those which are too soft are liable to render it sticky. The penetration of the asphalt may be adjusted to meet climatic conditions and the penetration range stated is to be considered as suggestive only.

It is an advantage of the general method herein described that it permits the readily available petroleum asphalts to be substituted, without loss of efficiency, for the often more costly and always more refractory wood or coal tars.

The metal soap may be a salt of copper, zinc, cadmium, mercury, chromium, cobalt, nickel or silver with naphthenic acids, resin acids or fatty acids such as oleic, stearic, lauric and palmitic. These metals may be described generically as the toxic heavy metals while the acids may be referred to generically as soap-forming organic acids.

Both the soap and the asphalt are substantially insoluble in water but are subject to aqueous emulsification. The soap only may be brought into aqueous solution by the use of ammonia or an amine, with or without the addition of a water-miscible solvent. In such solution the soap is an effective emulsifying agent for asphalt. The soap and the asphalt are mutually soluble at a temperature at which the asphalt is entirely fluid. Finally, either the asphalt alone or the blend of asphalt and soap is subject to emulsification in a variety of well known ways, some of which will be described.

The recital of these properties points to two basically distinct methods for preparing the aqueous treating agent, viz:

Method 1.—The soap may be brought into aqueous solution by the addition of ammonia or of a volatile amine and this solution mixed with a previously prepared aqueous emulsion of the asphalt;

Method 2.—The soap may be dissolved in the asphalt and the blend then emulsified with water containing ammonia or a volatile amine.

The distinction between these two methods, as regards the final result, is that in the first named the soap is carried in the aqueous phase and is precipitated on the surface of the fibre as the solubilizing agent (ammonia or amine) evaporates, while in the second the soap is partially carried in the bituminous phase and is precipitated with the asphalt when the emulsion "breaks" on contact with the surfaces of the fibres. The first method tends to enhance the bactericidal protection afforded by a given quantity of the toxic metal soap; the second to prolong the useful life of the soap at the expense of a reduction in its momentary activity.

In the application of method 1 above to the preparation of the treating liquid I proceed as follows:

(*a*) To a body of water is added ammonia or a water-soluble amine of reasonably rapid evaporation rate (preferably boiling above 15° C. and below 100° C.) and which is capable of forming a complex with the metallic ions of the soap to be used. Mono-, di- and triethylamine, normal and isopropylamine and the three butylamines

are suitable for this use and may be referred to generically as volatile aliphatic amines. While fully functional, there is no advantage in the substitution of the more costly amines for ammonia other than, in some instances, to slow down the precipitation of the soap which follows from evaporation of the solubilizing agent.

(*b*) The metal soap may be prepared in advance, by any of the conventional methods, or may be formed in situ. In the first case the soap may be dissolved in the ammonia or amine solution by prolonged contact or, more readily, by prior solution in a water-miscible solvent such as isopropyl or butyl alcohol. In the second case a water-soluble salt of the metal is added to the ammonia or amine solution to produce a metal-loamine complex, after which the organic acid is added.

(*c*) An aqueous emulsion of the asphalt is prepared in any conventional manner, preferably by a method which produces an emulsion which does not break too rapidly. For example, a thin stream of the molten asphalt may be introduced, with strong agitation, into a hot aqueous solution containing from 0.5% to 2.0% of ammonium oleate. The agitation is continued after the addition of the asphalt, if necessary, until the bitumen is completely and finely dispersed and the emulsion assumes a light brown color. The finished emulsion may contain more or less 50% by weight of asphalt, though this figure is far from critical. The ammonia soaps are preferred over the potassium or sodium soaps as they leave a residue which is free from tendency to re-emulsify. Any of the stabilizing agents of the prior art may be added to enhance the keeping quality of the emulsion if it is not to be used immediately. Casein or other protein is suitable for this purpose.

(*d*) The soap solution produced in step (*b*) and the emulsion produced in step (*c*) are then mixed in such proportions as to obtain the desired relation of metal to bitumen in the treating liquid. The following examples are typical of the above procedure:

Example 1.—Soap previously prepared

To a solution of 100 parts aqueous ammonia (28% NH_3) in 500 parts of water were added 100 parts of a solution of copper naphthenate in isopropyl alcohol, the concentration of this solution being equal to 9% copper content.

To this solution were added 200 parts of an aqueous emulsion of an 80/90 penetration asphalt having an asphalt content of 57%, stabilized by casein. The constituents of this mixture were blended by gentle agitation, giving a treating liquid of a concentration suitable for the treatment of fishing nets. All parts mentioned in this and the succeeding examples are by weight. The percentage composition of this product, as prepared and after application and evaporation of the volatile components, is as follows:

Copper naphthenate ---- per cent	8.8	40.8
Asphalt ---- do	12.7	58.8
Ammonium oleate ---- do	0.1	0.4
Isopropyl alcohol ---- do	2.3	
Casein ----	Trace	
Ammonia as NH_3 ---- per cent	3.1	
Water ---- do	72.0	

This or any other of the products of the examples may be further diluted with water if required.

Example 2.—Soap prepared in situ

To a solution of 100 parts of 28% aqueous ammonia in 400 parts of water were added 290 parts of an aqueous solution of copper sulfate containing 25% of the crystalline sulfate $CuSO_4.5H_2O$. To the solution thus obtained were added 155 parts oleic acid, after which the mixture was stirred until all components were in solution. To this mixture were added 300 parts of an asphalt emulsion containing 60% asphalt and the whole blended by stirring. The percentage composition, before and after drying, was as below:

Copper oleate ---- per cent	14.0	44.3
Asphalt ---- do	14.5	45.9
Ammonium sulfate ---- do	3.1	9.8
Ammonia as NH_3 ---- do	1.4	
Water ---- do	67.0	

A method which is intermediate between those described above as method 1 and method 2 consists in emulsifying separately the asphalt and a solution of the soap in a water-immiscible solvent. In this method a solution of previously formed soap in, for example, petroleum naphtha is strongly agitated with a cold aqueous solution of an amine or ammonia until finely dispersed, and the desired proportion of an asphalt emulsion such as that produced in (*c*) above is then mixed with this dispersion. The following is an example of this intermediate procedure:

Example 3.—Separate emulsification

To a solution of n-propylamine 100 parts in 450 parts of water were added 150 parts of a solution of zinc oleate in a volatile petroleum solvent containing 8% of zinc. The mixture was agitated until the petroleum solution was intimately dispersed in the amine solution. This dispersion was mixed with 200 parts of a soap-stabilized asphalt emulsion containing 45% of 80/90 penetration asphalt. The percentage composition of this product, before and after the evaporation of the volatile components, is as follows:

Zinc oleate ---- per cent	13.3	56.3
Asphalt ---- do	10.0	42.4
Ammonium oleate ---- do	0.3	1.3
Petroleum solvent ---- do	3.4	
Propylamine ---- do	11.2	
Water ---- do	61.8	

In the application of method 2 to the preparation of the treating liquid the procedure is as follows:

(*e*) An aqueous solution of ammonia or an amine is prepared as in (*a*) above;

(*f*) The asphalt is heated to a temperature at which it is completely fluid, as for example about 212° Fahr., and the soap blended with it. If the soap contains much water it will be necessary to use a slightly higher temperature and continue heating until the soap is at least partially dehydrated, permitting it to pass into solution in the asphalt;

(*g*) The asphalt-soap blend is then emulsified with a relatively small quantity of water containing either a preformed soap or a relatively non-volatile amine. In the latter case a corresponding quantity of a soap-forming fatty acid is incorporated in the blend (*f*) of asphalt and toxic metal soap. As this step of emulsification is necessarily performed at a temperature close to the boiling point of water, the use of ammonia or of a volatile amine will be found wasteful unless the emulsification is performed in a closed system;

(*h*) The concentrated emulsion produced in (*g*) is cooled to more or less atmospheric temperature and blended with such quantity of the ammonia or amine solution (*e*) as may be required to give the dilution desired for use.

Example 4.—Using preformed soluble soap

100 parts of 80/90 penetration asphalt were heated to 200° Fahr. and blended with 200 parts of zinc naphthenate previously prepared from naphthenic acids of an average molecular weight of 250. The blend was then emulsified, by agitation at about 200° Fahr., with 200 parts of a 1% aqueous solution of ammonium oleate, giving a concentrated fine dispersion. This product was cooled to about 80° Fahr. and blended with a solution of 100 parts 28% aqueous ammonia with 400 parts water. The percentage composition of this product, before and after evaporation, is as follow:

Zinc naphthenate	per cent	20.0	66.2
Asphalt	do	10.0	33.1
Ammonium oleate	do	0.2	0.7
Ammonia as NH_3	do	2.8	
Water	do	67.0	

Example 5.—Using soap-forming constituents

100 parts of 80/90 penetration asphalt were heated with 100 parts copper stearate and 10 parts stearic acid until mutually dissolved. The molten mixture was then added, with strong agitation, to a boiling solution of 5.5 parts triethanolamine (boiling point 277° C. at 155 mm.) in 200 parts water. The product was a finely dispersed concentrate which, after cooling, was blended with a solution of 80 parts 28% aqueous ammonia in 320 parts water. The percentage composition is as below:

Copper stearate	per cent	12.3	46.4
Asphalt	do	12.3	46.4
T-E-A stearate	do	1.9	7.2
Ammonia as NH_3	do	2.7	
Water	do	70.8	

In many instances the ammonia complex of the toxic metal soap is a sufficient emulsifying agent and in such cases the addition of a water soluble soap or its components, as in the above examples, may be dispensed with, the asphalt-toxic metal soap blend being dispersed directly in the ammonia or amine solution. In this practice it is desirable to dissolve the asphalt-soap blend in a water-miscible solvent, for example isopropyl alcohol or one of the butyl alcohols. By this means the emulsification can be brought about at normal temperatures and the excessive loss of ammonia or volatile amine incurred in agitating at high temperature is avoided.

Example 6.—Without adding soluble soap

100 parts petroleum road oil of 150/180 penetration were liquefied by gentle heating and blended with 100 parts of a solution of copper naphthenate in isopropyl alcohol, this solution containing 85% of the naphthenate. This blend was then dispersed in a solution of 100 parts 28% aqueous ammonia in 600 parts water, by agitation at atmospheric temperature. Percentage position:

Copper naphthenate	per cent	9.4	45.9
Bitumen	do	11.1	54.1
Isopropyl alcohol	do	1.7	
Ammonia as NH_3	do	3.1	
Water	do	74.7	

It will be understood that the examples above given are illustrative, not limiting, and that the formulation may be varied to suit the characteristics of the material to be treated, the environment in which the treated material is to be used, the nature of the most desired protection and the availability of the various alternative materials. Thus, while all of the examples refer to the use of petroleum residues as bitumens, the use of wood tars, coal tars, and the products of both is contemplated. Except as regards volatility and cost, ammonia and the various low-boiling amines are equivalent and may be substituted at will. The relation of bitumen to toxic soap may be increased in cases where the most weight is placed on resistance to abrasion and weathering and decreased in cases where protection against bacterial action is of more importance.

In all formulae, however, the content of ammonia or amine must be at least sufficient to form the water-soluble complex with the toxic metal soap. This quantity may readily be calculated from the combining weight of the selected metal by allowing one mol of ammonia for each equivalent weight of the metal and in addition X mols of ammonia, where X is the number of mols of ammonia required by each equivalent of the metal to form the ammonia complex.

It is permissible to replace the ammonium oleate or stearate disclosed above as emulsifying agents with other emulsifiers known in the art. Sulfonated vegetable or petroleum oils, in the form of their ammonia or amine salts, are particularly recommended for that purpose.

In the use of any of the above treating liquids the rope, twine, net or fabric is passed through a cold bath of the aqueous agent at such speed as to be saturated to the desired depth, after which it is drained and dried or allowed to dry. The ratio of bitumen to soap in the deposited film is controlled in the formulation of the treating liquid. The amount of bitumen + soap deposited may to some extent be controlled by squeezing or centrifuging the saturated product as it emerges from the bath, by regulating the speed of passage through the bath and, with more exactness, by varying the concentration of the bath. Any of the above liquids may be diluted with water to any desired degree, adding ammonia or amine if necessary to replace evaporation and thus to maintain solubility of the soap.

In draining back into the treating bath it will be remembered that bituminous emulsions break rapidly on contact with solid surfaces (the fibre surface) rather than by evaporation of the aqueous phase, while metallo-ammonium or amine complexes are resolved by evaporation of the amine constituent. It follows that the treating bath is more or less subject to progressive dilution and may need to be fortified from time to time by addition of a more concentrated liquid, particularly one richer in bitumen.

In the use of treating liquids prepared with ammonia or a highly volatile amine, instability may be incident to the evaporation of ammonia or amine from the bath. This lost amine content should be replaced at intervals.

Whichever method of preparation of the treating liquid may be adopted, the passage of the fibrous article through the bath and the subsequent drying produce the deposition on the fibre surfaces of a smooth, tough and pliable coating rich in bactericidal ingredients. The advantages of this general method as compared with the methods of the prior art may be summarized as follows:

a. The article treated is protected to a very high degree against bacterial action, abrasion and the effects of sunlight;

b. Such articles as cordage are penetrated much more deeply and rapidly by the aqueous emulsion than by hot tar or other bitumen as such;

c. The shrinkage incident to treatment is reduced to the order of 12% to 15% per dimension, materially less than that suffered in hot treatment;

d. As the treatment is performed in the cold, the deleterious effects of heat on the fibre are avoided;

e. The finished article is not tacky nor sticky but quite dry and easily handled, while on the other hand the stiffness of hot saturated products is avoided;

f. The weight increase due to the described treatment is usually about one-third that incident to hot saturation while at the same time to degree of protection afforded is materially increased.

g. The hydrolysis of the copper soap or other toxic metal soap is substantially inhibited by the presence of the bitumen and thus the bactericidal effect of the metal is preserved during a long period of use.

I claim as my invention:

1. A treating liquid for prolonging the life of articles composed substantially of vegetable fibre consisting substantially of a suspension of a bitumen in an aqueous solution of a soap of a complex ion formed of a bactericidal metal and a member of the group consisting of ammonia and the aliphatic amines boiling between about 15° and about 100° C. the weight relation between said bitumen and said soap being within the range from 3:1 to 1:3.

2. A treating liquid for prolonging the life of articles composed substantially of vegetable fibre consisting substantially of bitumen intimately dispersed in an aqueous medium containing in solution an unstable compound of a volatile alkaline agent with a soap of a bactericidal metal, the weight relation between said soap and said bitumen being not less than one to three.

3. A treating liquid for prolonging the life of vegetable fibres composed substantially of an intimate dispersion of a bitumen in an aqueous solution of an alkaline agent selected from the group consisting of ammonia and the aliphatic amines boiling between about 15° and 100° C., together with a soap of a bactericidal metal, said soap being initially present solely in said aqueous solution.

4. The method of producing a treating liquid for prolonging the life of articles composed substantially of vegetable fibre, which comprises: dissolving a soap of a bactericidal metal in an aqueous solution of an alkaline agent selected from the group consisting of ammonia and the aliphatic amines boiling between about 15° and about 100° C., and blending said solution with a previously prepared aqueous dispersion of a substantially soap-free bitumen.

HAROLD SCHILLER.