Patented Dec. 20, 1927. 1,653,010

UNITED STATES PATENT OFFICE.

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NITROCELLULOSE LACQUER.

No Drawing. Application filed July 23, 1926. Serial No. 124,549.

The object of my invention is to provide a nitrocellulose lacquer or varnish. Another object of my invention is to provide a nitrocellulose lacquer containing an ingredient which will serve to some extent as a substitute for castor oil and other substances which are used to produce films of high flexibility. Another object of the invention is to produce a nitrocellulose lacquer ingredient which may be used as a substitute, in whole or in part, for amyl or butyl acetates and which can be produced more cheaply, thereby effecting a saving in the cost of manufacturing the lacquer.

Pine oil is known to be a complex mixture of different substances, including terpineol, methyl chavicol, borneol, fenchyl alcohol, terpene hydrocarbons and smaller amounts of several other bodies. Pine oil itself has no colloiding action upon nitrocotton, and its individual constituents also possess little colloiding power. However, certain of these constitutents, notably borneol and fenchyl alcohol, yield, on oxidation, the ketones camphor and fenchone respectively, the former being a well known colloiding agent for nitrocellulose.

Pine oil contains about five per cent of borneol, and approximately as much fenchyl alcohol. These two alcohols cannot be easily isolated from pine oil in a high degree of purity by means of fractionation because of the nearness of their boiling points with those of some of the other constituents of pine oil.

As set forth in patent applications filed by me November 22, 1924, Serial No. 751,682, and August 17, 1925, Serial No. 50,839, of the latter of which this application is a continuation in part, it has been found feasible to treat pine oil with certain oxidizing agents and obtain a liquid, which may be designated oxidized pine oil, which exhibits considerable colloiding action on nitrocellulose. When pine oil is oxidized under proper conditions, it may contain approximately ten per cent of the ketones camphor and fenchone and, in addition, small amounts of other oxidized substances which colloid nitrocellulose. Another portion of the pine oil is oxidized to inert bodies, but the operation may be so conducted that a great portion of the pine oil remains unaltered, serving as a diluent to the active colloiding agents but possessing a strong solvent power for resins.

A solution of nitrocellulose may be prepared in straight oxidized pine oil, but on account of the rather high boiling range of oxidized pine oil, which is comparable to that of pine oil itself, it is usually desirable to add large proportions of lower boiling liquids. The latter may be either solvents or non-solvents for nitrocellulose. Examples of solvents are acetone and butyl acetate, and of non-solvents, alcohol and benzene. It is possible to incorporate a large proportion of a non-solvent in the vehicle without precipitating the nitrocellulose. Alcohol, even if it contains as much as five per cent of water, is found to be a desirable diluent from the standpoint of increasing the colloiding action of oxidized pine oil. Even if as much as several volumes of alcohol are added, the colloiding action of oxidized pine oil is accelerated to a remarkable degree.

Several oxidizing agents have been employed in preparing oxidized pine oil. Nitric acid is well adapted for use on a fraction of pine oil that is rich in fenchyl alcohol. Sodium or potassium bichromate, or chromic acid, is preferable in some respects to nitric acid, since the latter converts much of the pine oil into undesired products. I have employed other oxidizing agents such as chlorine, potassium permanganate and sodium hypochlorite, as well.

According to one method of oxidizing pine oil, as described in both of said prior patent applications, the pine oil is treated with 4.2 times its weight of an oxidizing mixture consisting of 15% sodium bichromate, 20% of sulfuric acid of 66° Bé. and 65% of water, but different proportions of the oxidizing agent, as well as varying amounts of acid and water, may be employed. Agitation is employed at a temperature of 21–32° C., with some cooling, since the reaction is exothermic, but the temperature may be allowed to rise somewhat higher. The crude oxidized oil is then refined by a steam distillation.

In both of said prior patent applications,

it is also stated that treating oxidized pine oil with a suitable dehydrator results in the conversion of a large part (say 60 per cent) of the oxidized pine oil into a lower boiling product, which, if desired, may be distilled off, leaving a residue comprising about 35 per cent of the original pine oil. As a typical example, it is stated that pine oil, oxidized as described, is heated for one and one-half hours to 150° C. with two per cent of fuller's earth. The fuller's earth is then separated from the liquid, and the latter is distilled and collected in one lot. The product may be designated type A. It may be used in lacquers in much the same manner as any other oxidized pine oil, being blended with non-solvent diluents and permissibly with other nitrocellulose solvents.

The advantages of type A over simple oxidized pine oil are:

(1) Greater volatility.

(2) Better solvent action on nitrocellulose in certain solvent mixtures.

(3) Greater freedom from blushing in lacquers.

It is, however, a poorer solvent for certain resins than straight oxidized pine oil.

The following is a comparison of the boiling ranges of typical samples of simple oxidized pine oil and type A—

	Oxidized pine oil	Type A
	°C.	°C.
5% over at	186	176
20% over at	198	180
50% over at	208	186
70% over at	210	190
90% over at	215	210

They differ chemically chiefly in the fact that part or all of the alpha-terpineol (b. p. 218° C.) in oxidized pine oil is converted into lower boiling substances (b. p. 170–185° C.) when type A is prepared.

These lower boiling substances consist largely of terpene hydrocarbons, dipentene and others. The alpha-terpineol which is present in oxidized pine oil has little colloiding action on nitrocellulose. The active colloiding ingredients in oxidized pine oil (camphor, fenchone, etc.) are not injured if the dehydration treatment be properly applied.

An alternative way of preparing type A comprises the following steps:

(*a*) The pine oil is treated with a dehydrating agent, thereby converting all or part of its terpineol content into lower boiling point substances, but with a minimum amount of dehydration of the remaining constituents.

(*b*) Forty to seventy-five per cent of the product is removed by distillation, preferably by using a fractionating column.

(*c*) The residual pine oil is oxidized in the manner set forth in my earlier application and as hereinbefore described or in any other efficient way.

(*d*) The oxidized residual pine oil is then refined by steam distillation.

(*e*) The refined oxidized residual pine oil may be then added to part or all of the distillate from step (*b*), thereby obtaining the product hereinbefore designated as type A having a boiling range approximating that hereinbefore specified for type A.

However, the oxidized residual pine oil resulting from step (*c*) may be employed alone.

One particular way of practicing the modified process just described is as follows: The pine oil is heated to 145° C. for one hour with one and one-half per cent of fuller's earth. After separating the fuller's earth, sixty per cent of the charge is distilled off through a fractionating column. The residue is then oxidized as hereinbefore described. The crude product is refined by steam distillation and is then blended with the first distillate.

Any reagent whose chief effect is that of splitting off chemically combined water from certain of the pine oil constituents, notably terpineol, may be used as a dehydrating agent. While a wide variety of dehydrators may be employed, it is preferable to use one which decomposes the terpineol without attacking the other constituents. Mineral acids, e. g. dilute sulfuric acid, acid salts (e. g. sodium bisulfate), salts which give an acid reaction on hydrolysis (e. g. copper sulfate), small amounts of iodin or bromin, or various substances which dehydrate by virtue of surface catalysis, may be employed. The latter class includes activated carbon, fuller's earth, kieselguhr, and in some instances other argillaceous or silicious earths.

In place of starting with pine oil as the raw material, I may use the by-product oil that is obtained in preparing terpin hydrate from pine oil.

The oxidized and dehydrated pine oil products resulting from the foregoing processes which comprise (in the order stated or the reverse order) partial oxidation of oxidizable constituents of pine oil and dehydration to convert such constituents into a lower boiling product have, except for their lesser capacity to dissolve certain resins, all the advantages of oxidized pine oil products produced by simple oxidation of their oxidizable constituents, and in addition have the advantages, hereinbefore mentioned, of greater volatility, better solvent action on nitrocellulose in certain solvent mixtures, and greater freedom from blushing in lacquers; and are therefore preferred by many users.

Type A, like straight oxidized pine oil, will contain a proportion of oxidized inert bodies, serving as diluents, and in preparing

the nitrocellulose solution, it is usually desirable, as when using straight oxidized pine oil, to add rather large proportions of lower boiling liquids, which may be solvents or non-solvents for nitrocellulose.

The invention forming the subject-matter of this application does not comprehend a nitrocellulose lacquer with oxidized pine oil, broadly, since the same forms the subject-matter of the earlier of the hereinbefore specified prior patent applications, but is intended to comprehend any nitrocellulose lacquer comprising a solution of nitrocellulose with dehydrated and oxidized pine oil (the preponderating proportion of whose constituents have, preferably, a boiling range of 175–220°) and also such a solution with a diluent having a substantially lower boiling range than the boiling range of oxidized pine oil. More specifically, the present invention is intended to comprehend compositions like the following typical composition, which is submitted as a specific illustration or preferred embodiment of the broad invention:

Ingredients.	Percentage.
Low viscosity nitrocotton	10.5
Denatured alcohol	4.5
Benzene	26
Butanol	5
Ethyl acetate	6
Butyl acetate	16.5
Gum solution	16.5
Diethyl phthalate	5
Dehydrated and oxidized pine oil	10

Dehydrated and oxidized pine oil is intended to include pine oil certain of whose oxidizing constituents are oxidized even though some of its constituents may not be oxidized or oxidizable.

Substantially all the advantages of the foregoing specific composition may be attained with other compositions containing 1–20% of dehydrated and oxidized pine oil, 5–20% of low viscosity nitrocotton, 10–30% of aliphatic alcohols, 5–30% of esters, 10–50% of aromatic hydrocarbons, and 5–20% of gum solutions (preferably about 50% gum), and approximately 5% of plasticizer.

Where reference is made to a nitrocellulose lacquer, I do not mean to include only those lacquers which contain resins, as the oxidized product is also applicable as a nitrocellulose solvent when resins are not present in the solution, and in fact, in the latter case, the product embodying my invention is of special advantage.

Having now fully described my invention, what I claim and desire to protect by Letters Patent is:

1. A nitrocellulose lacquer including a solution of nitrocellulose and containing dehydrated and oxidized pine oil constituents.

2. A nitrocellulose lacquer including a solution of nitrocellulose and dehydrated and oxidized pine oil constituents, and one or more diluents having a substantially lower boiling range than the boiling range of oxidized pine oil.

3. A nitrocellulose lacquer comprising a solution of nitrocellulose and dehydrated and oxidized pine oil the preponderating proportion of whose constituents has a boiling range of approximately 175–220° C.

4. A nitrocellulose lacquer including a solution of nitrocellulose containing from about one per cent to twenty per cent of dehydrated and oxidized pine oil.

In testimony of which invention, I have hereunto set my hand, at Kenvil, N. J., on this 6th day of July, 1926.

IRVIN W. HUMPHREY.