Patented July 19, 1949 2,476,879

UNITED STATES PATENT OFFICE

2,476,879

METHOD FOR SOLUBILIZING INSOLUBLE GELATINIZED OILS

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No Drawing. Application May 16, 1947, Serial No. 748,665

15 Claims. (Cl. 106—243)

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This invention relates to the solubilizing of insoluble, gelatinized fixed oils, such as vegetable, animal, or synthetic oils or mixtures of derivatives of such oils or of such oils with other materials and has particular relation to a process of solubilizing such insoluble gelatinized materials so that they can be made useful in oleo- or oleo-resinous compounds, in varnish, lacquer, coating, extrusion, covering, impregnation, insulation compounds or the like. The present application is a continuation-in-part of my copending allowed application Serial No. 496,262 (now abandoned).

It is known that the most desirable bases for use in preparing coating compositions are those which produce coatings having a minimum degree of swelling. The swelling capacity of a material is characterized by the fact that the swelling is connected with an increase in volume and the deswelling, i. e., shrinking, is connected with a decrease in volume. Thus it is general practice in the coating art to avoid the use of varnishes, oils, lacquers, or similar compounds which are in a swollen condition. (Fixed oils are defined in Hackh's Chemical Dictionary, second edition, 1937, as those oils which consist of the fatty substances of vegetable and animal organism and contain the esters of fatty acids.) For example, fixed oils which can be readily transformed as by polymerization, or by the application of heat, by distillation or by chemical action into a paritially insoluble condition and having some swelling ability, are generally used in a non-gelatinous condition. Thus gelatinized fixed oils have heretofore been of little use in the coating arts.

It has been observed that such materials which are used in a swollen condition, as for instance highly polymerized fixed oils, undergo shrinking while drying and that during the drying or in the shrunken condition, such materials lose most of their ability to swell, probably by virtue of oxidation, polymerization, or other chemical action. One possible explanation is that the components of such materials are apparently connected to each other in a special manner and in a different manner than are the molecules of other materials which are readily soluble in the usual thinners or varnish solvents.

An object of the present invention is to provide a process for treating insoluble, gelatinous, swollen oils so that they are capable of being applied by coating or covering methods, as by brushing, spraying, dipping, or extruding, and can further be compounded without the necessity of being returned to a non-swelling condition.

Another object of the invention is to provide a process for the preparation of a stable, soluble oil base composition having a high shrinkage capacity when dried from a state of solution.

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A further object of the invention is to provide a process for solubilizing a swelled, insoluble, gelatinous fixed oil base composition.

Still another object of the invention is to provide a process for modifying the coating characteristics of fixed oils so as to bring them into a swelling or swollen condition where they can be readily worked up or dissolved into a liquid state, and in which condition they can be stored indefinitely and then can be used directly and can be readily worked up or dissolved into a liquid state, and in which condition they can be stored indefinitely and then can be used directly and can be readily diluted for use as a coating composition.

A still further object of the invention is to provide a fixed oil base coating composition which will have desirable coating or covering characteristics, such as a high degree of elasticity, resistance to hardening, aging, changes in temperature and changes in humidity, and which can be modified by compounding with resins, asphalts, phenolic resins, alkyd resins and other synthetic resinous materials, copal gums, and the like.

Still another object of the invention is to provide a process for solubilizing gelatinized oleo compounds in the presence of natural gums, resins, asphalts and other natural materials thereby obtaining useful compounds of solubilized gels with the natural material.

Still another object of the invention is to provide a process for solubilizing those insoluble fixed oils which are incapable of forming coherent film-like substances, so that they may be used subsequently as film-forming coatings.

Still another object is to provide a process for solubilizing gelatinized oleo compounds in the presence of synthetic resinous compounds such as phenolic resins or alkyd resins thereby obtaining useful compounds of such solubilized gels with synthetic resinous materials.

Still another object is to provide a process for solubilizing gelatinized oleo compounds in such manner that the products can be dissolved in solvents and plasticizers for use in lacquers, cellulose derivatives and vinyl compounds, and can be dissolved readily in polymerizable liquids or solutions, such as styrene or the like to form stable solutions.

Another object of the invention is to provide a process for increasing the swelling capacity of swollen or swelling oils, to such an extent that they can be worked up in the usual thinners and varnish solvents.

These and other objects of the invention will be readily understood by reference to the following description:

I have discovered that metal soap-like reaction products, preferably formed by reacting a

fixed oil, a petroleum acid, a rosin acid, or mixture thereof with a compound of a metal capable of reaction with such oils, fatty acids, resin acids, naphthenic acids or other organic compounds to form a corresponding oil soluble metal soap-like reaction product can be used to solubilize and influence the degree of swelling of fixed oils which are at least partially insoluble and in a stage of swelling or are partially swollen, or which are completely swollen and in an insoluble condition.

I have discovered further that gelatinized or at least partially insoluble oils can be solubilized by melting and compounding therewith certain metallic soap-like reaction products by subjecting the mixture to a melting temperature such that substantially the entire mass of the resulting composition is melted into the liquid stage thereby forming a soluble oil which is capable of forming a stable solution.

I have also discovered that the above-discovered process may be practiced with success by utilizing a metallic soap-like reaction product which is at least partially soluble in an oil and which is in a liquid state at the melting temperature of the above-set forth process.

According to my invention, fixed oils, which are insoluble or at least partially insoluble, may be solubilized by melting and reacting therewith, at a temperature below the decomposition temperature of the resulting compound, a metal soap-like reaction product.

By fixed oil I mean to include any oil which consists of the fatty substances of vegetable or animal organisms containing an ester of a fatty acid; or any fatty acids or their derivatives; or any synthetically produced oil containing an ester of a fatty acid; or any synthetically produced fatty acid oil-like ester.

By insoluble I mean to include the characterization of any compound which is incapable of dissolving in a liquid to form a stable homogeneous mixture.

By gelatinized I mean to include any fixed oil which is at least partially insoluble and which is capable of increasing its volume when contacted by a solvent (swelling capacity). In addition, I mean to include not only those gelatinized fixed oils which are film-forming but also those which are not capable of forming a film.

By solubilizing I mean to include the treatment of any insoluble or at least partially insoluble material to the extent that it will be capable of mixing with a liquid to form a stable, homogeneous solution.

By metal soap-like reaction product I mean to include any alkali, alkaline-earth, or heavy metal compound of a complex organic acid or ester thereof, which is at least partially soluble in a fixed oil.

By stable I mean to include any compound or solution which will remain in a balanced condition of miscibility which is not readily destroyed.

It is possible that the metal soap-like reaction products of the present invention may influence the degree of swelling without producing a chemical reaction. In preparing a contact substance; that is, a metal soap-like reaction product in accordance with the present invention oils or their acids or mixtures of such materials are treated in the presence of compounds such as metallic peroxides, acetates, oxides, hydroxides, carbonates, borates, or other inorganic or organic metal salts, at a temperature which is sufficiently elevated to cause a reaction to take place between the oil and the metal compound so as to form the corresponding metal soap-like reaction product. The resulting reaction product is clearly distinguished from other chemical substances by its ability to raise the swelling capacity of insoluble, gelatinous swollen or swelling oils, when compounded therewith, to such an extent that the resulting composition can be worked up in the usual thinners or varnish solvents. It will be understood that the insoluble, gelatinous swollen or swelling oils which are treated with the metal soap-like contact substance in accordance with the present invention may result from heating, distillation, polymerization, oxidation, condensation such as the phthalic acid reaction, the action of sulphur, or of accelerators such as sulphur chlorides, boron fluorides, tin tetrachlorides, or other chemical action, or from various combinations of such reactions.

The exact nature of the compounding of the contact substance with the insoluble, gelatinous swelling or swollen fixed oil is not clearly understood. However, it is believed that the compounding results in the formation of a solution or in the formation of a condition of unlimited swelling. It has been found that alkali, alkali-earth, and heavy metals selected from each of the groups of the periodical system may be utilized to form metallic soap-like reaction products which may be used successfully as contact substances in practicing the present invention.

In the practice of the present process the relation between the insoluble gelatinized, swelling oil and the contact substance depends in part upon the degree of swelling of the insoluble, gelatinized oil. If the gelatinized oil is in condition to be readily swelled, only a minimum amount of contact substance is required; whereas a greater amount is necessary if the gelatinized oil is in a condition which may not be readily swelled. Thus, it has been found that fresh gelatinized oils require a smaller proportion of contact substance than is required for gelatinized oils which are in an aged condition. Likewise, certain oils, which have been highly gelatinized by continued heating, distillation or vacuum treatment, require an increased amount of contact substance. Oils which have been altered or modified by the removal of the non-gelatinized components also require an increased amount of contact substance.

While it has been found that an excess amount of contact substance may be used for obtaining certain desired characteristics, the proportions set forth in the following examples are preferred.

In a further embodiment of the invention, it has been found that the process of liquifying the gelatinous compound with a metal soap-like reaction product may be promoted or accelerated by adding a non-gelatinous oil or other material which is liquid at the temperature of the reaction and has the properties of acting as a solvent for the metal soap-like reaction product and as a sweller for the gelatinous compound.

In another embodiment of the invention, it has been found that free acids contained in the soap-like reaction products may be removed or neutralized by heating them with borates, such as manganese or calcium borate and that such treatment does not interfere with the nature of the liquified gelatinous material.

It further has been found that sedimentations or impurities can be removed by filtering, settling or centrifuging without thereby removing the liquified gelatinous material from the compound.

It further has been found that the process of compounding the gelatinous compounds with the metal soap-like reaction product may be accompanied by a secondary process. Thus, in liquifying gelatinous products containing sulphur with metal soap-like reaction products, the process of liquifying proceeds parallel with the forming of metal sulphides which can be removed subsequently from the liquifaction.

It will be seen from the following examples that they relate to a preferred process for the preparation of the metallic soap-like reaction products which are used as a contact substance for solubilizing the swelled, insoluble gelatinous oil.

Certain examples relate to a preferred process for preparing swollen, insoluble, gelatinous fixed oils, although it will be understood that any swollen, insoluble, gelatinous fixed oils resulting from other processes may be used.

Other examples relate to a preferred process for solubilizing a swollen, insoluble, gelatinous oil or oil base, by treating the gelatinous oil with contact substances, wherein such process is performed in the presence of materials, which are neither a component part of the gelatine nor a component part of the contact substance, nor a non-gelatinous form of a gelatinous oil material.

The following working examples illustrate the preferred conditions and compounds which may be utilized in practicing my invention but it will be understood that the scope of the invention is not confined thereto:

PREPARATION OF THE METALLIC SOAP-LIKE REACTION PRODUCT CONTACT SUBSTANCE

I. Fixed oils
  A. Vegetable oils.
    1. Drying oils.

Example 1

About 93 parts by weight of linseed oil was heated in a reaction kettle. When the heated oil attained a temperature ranging from 150 to 200° C., about 1.5 parts by weight of cobalt acetate was added slowly, with stirring, to the kettle. It was noted that the linseed oil raised up in the kettle during the reaction and during the escaping of the by-products, which probably included acetic acid, as the reaction product was eventually freed from the acetate used. Heating of the reaction product, which was a soluble cobalt linseed oil reaction product, was then continued until the temperature thereof was above 200° C. and the temperature was so maintained until the reaction was completed.

Example 1a

In place of the cobalt acetate used in Example 1, about 2.5 parts of iron acetate or corresponding quantities of cobalt or iron oxide were used as the compound capable of reacting with the oil to form the corresponding metal soap-like reaction product.

Example 2

Similarly as in Example 1 above, in the following examples drying oils and metal compounds

were reacted to form metal soap-like reaction products. It was found preferable to use about 1–5% by weight of metal compounds to 100 parts of oil. The temperatures used were substantially those used in Example 1.

(*a*) 93 parts of linseed oil and 4 parts lead acetate.
(*b*) 93 parts of soyabean oil and 4.2 parts cobalt acetate.
(*c*) 93 parts of perilla oil and 6.2 parts cupric acetate.
(*d*) 93 parts of linseed oil and 5.4 parts aluminum acetate.
(*e*) 93 parts of linseed oil and 2 parts of cobalt oxide.
(*f*) 93 parts of linseed oil and 3 parts of iron oxide.
(*g*) 93 parts of perilla oil and 11.5 parts zinc sulphate.
(*h*) 93 parts of perilla oil and 9.3 parts silver nitrate. (A surplus of the silver nitrate salt remained after cooling as a solid at the bottom of the container.)
(*h'*) 93 parts linseed oil and 13 parts ZnO_2(55%).

2. Semi-drying and non-drying vegetable oils.
(*i*) 93 parts cashew nut shell liquid and 4.8 parts cobalt acetate. About 13% of the liquid evaporated during the treatment.
(*j*) 93 parts of cottonseed oil and 7.7 parts cobaltous nitrate.

B. Animal oils.
(*k*) 93 parts of light (menhaden) fish oil with 12.4 parts nickel formiate. (After heating up to 280° C. some surplus sediment remained.)
(*l*) 93 parts of cod liver oil and 3.1 parts of lead acetate.

C. Synthetically modified and produced oils.
(*m*) 93 parts of dehydrated castor oil and 2.8 parts of cobalt acetate.
(*n*) 93 parts of conjugated linseed oil and 3.5 parts of cobalt acetate.
(*o*) 93 parts of commercial synthetic oil produced by the esterification of fatty acids ("Neo-fat 190") and 4.6 parts nickel formiate.

D. Oil distillation.
(*p*) 93 parts of distillate from cottonseed oil and 6 parts of cobalt acetate.
(*q*) 31 parts of distillate from perilla oil, 62 parts of additional perilla oil and 4.6 parts of cobalt acetate.

E. Fatty acids.
(*r*) 93 parts of oleic acid and 20 parts of zinc benzoate. (Heated up to about 185° C. at which temperature much of the benzoic acid escaped.)
(*s*) 93 parts of oleic acid and 20 parts of lead hydroxide. (Heated up to about 185° C.)
(*t*) 93 parts of linoleic acid and 2.15 parts basic bismuth acetate.
(*u*) 93 parts linoleic acid and 2.4 parts chromium carbonate.
(*v*) 93 parts linoleic acid and 2.8 parts manganese acetate.

II. Rosin acids.
(*w*) 93 parts rosin oil and 2.35 parts cobalt acetate.

III. Petroleum acids.
(*x*) 93 parts naphthenic acid and 2.79 parts cobalt acetate.

IV. Mixtures of the compounds set forth in Examples 2*a*–2*x*.
(*aa*) 43 parts soy bean oil,
50 parts linseed oil and
2.5 parts cobalt acetate.
(*bb*) 93 parts linseed oil,
2 parts cobalt acetate and
1 part iron oxide.
(cc) 77.5 parts bodied linseed oil,
15.5 parts oleic acid and
1.6 parts cobalt acetate.
(*dd*) 77.5 parts heat-bodied linseed oil,
15.5 parts rosin acid and
2 parts cobalt acetate.
(*ee*) 47 parts linseed oil,
46 parts rosin oil and
2 parts cobalt acetate.
(*ff*) 70 parts linseed oil,
23 parts stearic acid and
2.35 parts basic bismuth acetate.
(*gg*) 70 parts linseed oil,
23 parts naphthenic acid and
2.4 parts cobalt acetate.

PREPARATION OF THE INSOLUBLE SWELLING GELATINOUS OIL

Example 3

Raw linseed oil was heated in a reaction kettle to a temperature ranging from about 285 to 290° C. for the promotion of the polymerization, air was directed through the linseed oil as a contact agent, although oxygen may also be directed through the oil for the same purpose. The reaction is generally completed by the heat generated by the reaction, which ordinarily causes a 20° C. rise in temperature. If the self-heating does not occur readily, the reaction kettle should be further heated until a temperature has been reached where the final gelatinizing effect occurs. This gelatinizing effect can be readily recognized by the fact that the oil loses its liquid characteristics and turns gelatinous. Heating was discontinued as soon as the gelatinizing effect had occurred. Upon cooling, the swelled insoluble gelatinous, viscous oil resulting from the heating, further solidified into a viscous elastic compound, which could be stretched; i. e., extended, and which exhibited resistance to being torn apart.

In place of the raw linseed oil, a pretreated, preheated, and bodied linseed oil, and a mixture of such oils, plus a drier or resin, were also used.

Example 4

The process of the preceding example was followed to obtain gelatinization and insolubilization of the following oils:

(a) Soy bean oil.
(b) Perilla oil.
(c) A mixture of 4 parts soy bean oil and 1 part China-wood oil.
(d) A mixture of 2 parts cashew nut shell oil and 1 part China-wood oil.
(e) Norwegian cod liver oil.
(f) Light menhaden fish oil.
(g) China-wood oil.

Example 5

(a) Dehydrated castor oil (gelatinizing temperature of 300° C. used).
(b) Synthetic drying oil (gelatinizing temperature of about 270° C. used) ("Neo-fat").
(c) Synthetic oil (gelatinizing temperature of about 280° C. used) ("Trimol").

Example 6

100 parts commercial refined, bodied linseed oil was mixed with 8–10 parts commercial t-butyl-hydro-peroxide and heated. At around 150° C., strong gas formation occurred and gelatinization took place between 200 and 230° C.; that is, considerably below the gelatinization temperature of raw linseed oil. The gel was light in color.

Example 7

Gelatinized oils were also obtained by distilling off the non-gelatinizing portions of various oils. This was accomplished under diminished pressure by continuing the distillation at about or slightly above 270° C. until the desired degree of gelatinization occurred.

(a) 100 grams bodied linseed oil was distilled in vacuum until gelatinization occurred. 81.8 grams gel were obtained.
(b) 100 grams cottonseed oil was distilled in vacuum until gelatinization occurred. 41 grams gel were obtained.
(c) 100 grams perilla oil was distilled in vacuum until gelatinization occurred. 80.8 grams gel were obtained.
(d) 100 grams light Norwegian menhaden fish oil were distilled in vacuum until gelatinization occurred. 43.5 grams of gel were obtained.
(e) 100 grams modified (dehydrated) castor oil were distilled in vacuum until gelatinization occurred. 48 grams gel were obtained.

Example 8

A gelatinized oil was obtained by chemical action by heating 40 grams linseed oil to a temperature of about 50 to 100° C. About one part of boron trifluoride gas was added to the oil under stirring until gelatinization occurred. The mixing of the boron trifluoride with oil also was accomplished at a lower temperature and the mixture then heated so that an at least partially insoluble gel condition was obtained. The gel was washed with water for removal of the water soluble products.

(a) In a further example, 3 parts of a mixture of 1 part boron trifluoride etherate with 2 parts solvent was added in place of the boron trifluoride gas.

Example 9

45 parts of linseed oil were mixed with 10 to 20 parts of tetrachloro-phthalic-anhydride. The mixture was heated to about 200° C. until gel forming began. 20 more parts of oil were added and heating was continued until an at least partially insoluble oleo-gel had been formed. The material was then washed with water for removing water-soluble products.

Example 10

In the following examples, oil-modified alkyd resins (commercial combinations of oils or oil-acids with reaction products of phthalic anhydride and glycerols) were gelatinized according to the process set forth in Example 3.

(a) 100 parts commercial long-oil-alkyd resin known as "Rezyl X–315" was heated at about 270° C. gelatinization occurred. About 64.4 parts gelatinous substance was obtained.
(b) 100 parts long-drying alkyd resin known as "Glyptal 2466" obtained from the 70% commercial solution was heated to about 280° C. About 80 parts of gelatinous substance was obtained.
(c) 100 parts of medium oil oxidizing alkyd resin known as "Rezyl 412–1" obtained from the 50% commercial solution was heated at about 220° C. until gelatinization occurred. About 87 parts gelatinous substance was obtained.

SOLUBILIZING THE SWELLED, INSOLUBLE, GELATINOUS FIXED OIL BASE

Example 11

40 parts by weight of the insoluble gelatinous linseed oil base made in accordance with the process set forth in Example 3 above was melted together with about 10 parts by weight of the metal soap-like reaction product obtained in accordance with the process set forth in Example 1. The melting temperature of the swelled insoluble gelatinous linseed oil base varies in accordance with its condition and age. However, it has been found that an average temperature of about 250° C. may be used as a melting temperature. Melting is complete when the composition has become uniform throughout. The resulting product is in the form of a stable, soluble, linseed oil base composition having a high shrinkage capacity when dried from a state of solution. The resulting composition may be stored with great resistance to aging and it may be thinned with various quantities and various types of solvents or mixtures of solvents. In this condition it may be combined with natural or synthetic resins, asphalts, copal gums or solutions thereof. In addition, it may be readily melted with either natural or synthetic resins, asphalts, or copal gums.

While preferred heating temperatures for the treating, compounding, and gelatinizing have

been set forth in the foregoing examples, it will be understood that temperatures will vary in accordance with the physical condition, age, and types of compositions employed.

	Gelatinized oil	Contact substance
a	20 parts linseed oil	10 parts obtained from reacting 93 parts linseed oil and 4 parts lead acetate.
b	do	7 parts obtained from reacting 77.5 parts linseed oil, 15.5 parts oleic acid and 1.6 parts cobalt acetate.
c	do	5 parts obtained from reacting 77.5 parts linseed oil, 15.5 parts resin acid and 2 parts cobalt acetate.
d	do	5 parts obtained from reacting 93 parts perilla oil and 62.2 parts cupric oxalate.
e	do	6.2 parts obtained from reacting 93 parts perilla oil and 11.2 parts zinc sulfate.
f	do	5 parts obtained from reacting 93 parts cottonseed oil and 7.7 parts cobaltous nitrate.
g	do	6 parts obtained from reacting 93 parts cashew nut shell oil and 4.8 parts cobalt acetate.
h	do	5.5 parts obtained from reacting 93 parts light menhaden fish oil and 12.4 parts nickel formiate.
i	do	5 parts obtained from reacting 93 parts modified (dehydrated) castor oil and 2.8 parts cobalt acetate.
	do	6 parts obtained from reacting 37 parts linseed oil, 46 parts rosin oil, and 2 parts cobalt acetate.
k	do	5.5 parts obtained from reacting 93 parts linoleic acid and 2.15 parts bismuth acetate (basic).
l	do	5.5 parts obtained from reacting 93 parts linoleic acid and 2.4 parts chromium carbonate.
m	do	5.5 parts obtained from reacting 70 parts linseed oil, 23 parts naphthenic acid and 2.4 parts cobalt acetate.
n	do	7.5 parts obtained from reacting 70 parts linseed oil, 23 parts stearic acid and 2.35 parts bismuth acetate (basic).
o	do	6 parts obtained from reacting 93 parts linoleic acid and 2.8 parts manganese acetate.
p	do	6 parts obtained from reacting 93 parts resin acids in the form of rosin oil and 2.35 parts cobalt acetate.
q	do	5.6 parts obtained from reacting 93 parts naphthenic acids and 2.8 parts cobalt acetate.
q'	20 parts China-wood oil-gel	10 parts obtained from reacting 93 parts China-wood oil and 5 parts cobalt acetate.
q''	39 parts China-wood oil-gel	20 parts dibutyl tin dilaureate and 15 parts naphthenic acid.
r	20 parts perilla oil-gel	5.6 parts obtained from reacting 93 parts perilla oil and 9.3 parts silver nitrate.
s	20 parts soy bean oil-gel	10 parts obtained from reacting 93 parts soy bean oil and 4.2 parts cobalt acetate.
t	20 parts gel from 4 parts China-wood oil, 16 parts soy bean oil	10 parts obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.
u	20 parts perilla oil-gel	3 parts obtained from reacting 93 parts perilla oil and 9.3 parts silver nitrate. 2 parts obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.
v	20 parts cod liver oil-gel	10 parts obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.
w	20 parts light menhaden fish oil-gel	7.2 parts obtained from reacting 93 parts cod liver oil and 3.1 parts lead acetate.
x	20 parts gelatinized dehydrated castor oil	8 parts obtained from reacting 93 parts dehydrated castor oil and 2.8 parts cobalt acetate.
y	20 parts gelatinized synthetic drying oil	10 parts obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.
z	do	11 parts obtained from reacting 93 parts synthetic drying oil and 3.5 parts cobalt acetate.
aa	20 parts gelatinized synthetic oil	10 parts obtained from reacting 93 parts synthetic oil and 4.6 parts cobalt acetate.
bb	20 parts light colored gelatinized linseed oil obtained from reacting 105 parts linseed oil and 8–10 parts t-butyl-hydroperoxide at about 200–235° C.	6 parts obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.
cc	20 parts light colored gelatinized linseed oil obtained from reacting 105 parts linseed oil and 8–10 parts t-butyl-hydroperoxide at about 200–235° C.	10 parts obtained from reacting 93 parts linseed oil and 3.1 parts chromium carbonate.
ccc	61 parts linseed oil-gel	26 parts obtained from reacting 93 parts linseed oil and 13 parts ZnO_2 (55%).
dd	20 parts gelatinized linseed obtained by diminished pressure	8 parts obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.
ee	20 parts gelatinized perilla oil obtained by distillation under diminished pressure.	6.1 parts obtained from reacting 62 parts perilla oil, 31 parts distillate of perilla oil and 4.5 parts cobalt acetate.
ff	20 parts gelatinized cottonseed oil obtained by distillation under diminished pressure.	10 parts obtained from reacting 93 parts distillate of cottonseed oil and 6 parts cobalt acetate.
gg	20 parts gelatinized light menhaden fish oil obtained by distillation under diminished pressure.	14 parts obtained from reacting 93 parts dehydrated castor oil and 2.8 parts cobalt acetate.
hh	20 parts gelatinized synthetic dehydrated castor oil obtained by distillation under diminished pressure.	13.3 parts obtained from reacting 93 parts dehydrated castor oil and 2.8 parts cobalt acetate.
ii	20 parts gelatinized mixture obtained from a distillation under diminished pressure of a mixture of 2 parts China-wood oil and 1 part soy bean oil (28 grams mixture).	10 parts obtained from reacting 10 parts linseed oil, 2 parts oleic acid and 0.2 part cobalt acetate.
jj	20 parts gelatinized mixture obtained from distillation under diminished pressure of 27 grams of a mixture of 3 parts conjugated linseed oil and 1 part cottonseed oil.	10 parts obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.

Example 12

The process set forth in Example 11 was followed in solubilizing the insolubilized oils of Example 3 with the soap-like reaction products of Examples 1–2. The fixed oil reaction products in accordance with the following examples readily dissolved in equal parts of toluene and stable solutions were thereby obtained.

20 parts commercial linseed oil gel containing 15% volatile matter.	8 parts contact material obtained from reacting 93 parts linseed oil and 1.5 parts cobalt acetate.

Example 13

This exemplifies the process of Example 11, as applied to commercial gels derived from vegetable, animal or synthetic oils (including those derived from mineral oils) or mixtures, containing the same and using any of the contact materials made according to Example 1 and 2.

Example 14

In this example, the process set forth in Example 11 was modified by having it take place in the presence of an added compound which is (1) a liquid at the solubilizing reaction temperature, (2) a solvent for the contact substance and (3) a swelling agent for the gelatinous material. In this manner, heavy-bodied gels and heavy-bodied contact substances may be obtained.

	Oil-gel	Contact substance	Added Compound
a	20 parts heavy linseed oil gel	10 parts obtained from 93 parts linseed oil and 5.5 parts basic aluminum acetate (a nearly solid reaction product).	4 parts non-gelatinous, bodied linseed oil.
b	20 parts heavily gelatinized perilla oil.	6.6 parts obtained from 93 parts linseed oil and 1.5 parts cobalt acetate.	1 to 4 parts non-gelatinous perilla oil.
c	20 parts heavy gel obtained from 20 parts cashew nut shell and 10 parts China-wood oil.	20 parts obtained from 93 parts dehydrated castor oil and 2.8 parts cobalt acetate.	10 parts dehydrated castor oil.
d	20 parts obtained from conjugated linseed oil.	11 parts obtained from 93 parts dehydrated castor oil and 2.8 parts cobalt acetate.	4 parts conjugated linseed oil.

Example 15

This exemplifies the process of Example 11 as applied to gelatinous oil products obtained by chemical action like those produced in Examples 8 and 9 using the contact substances set forth in Examples 1 and 2.

	Oil-Gel	Contact substance	Added Compound
a	20 parts linseed oil produced with boron trifluoride etherate (See Example 8).	32 parts of a mixture containing equal parts of a reaction product obtained from 93 parts linseed oil and 1.5 parts cobalt acetate, and from 93 parts oleic acid and 20 parts zinc benzoate.	3.2 parts linseed oil.
b	20 parts linseed oil gel produced with tetrachlorophthalic anhydride (See Example 9).	20 parts obtained from 93 parts linseed oil and 1.5 parts cobalt acetate.	2.4 parts linseed oil.

Example 16

This exemplifies the process set forth in Example 11, as applied to oleo-gels, known as "vulcanized oils" or as "factice materials" or as "rubber substitutes" obtained by the effect of sulphur ("brown" material) or sulphur chlorides ("white" material) or other vulcanizing agents (e. g. "amber" material), using any of the contact materials made in accordance with Examples 1 and 2. It was noted that in an accompanying secondary reaction, a sedimentation of metal sulphides occurred frequently and became visible, particularly in the thinned solution. The sedimentation was separated by usual methods and did not interfere with the solubilizing itself.

	Vulcanized Oil Product	Contact Substance
a	20 parts white vulcanized oil produced from rapeseed oil treated with sulphur chloride.	10 parts obtained from reacting 93 parts oleic acid and 20 parts zinc benzoate.
b	20 parts brown vulcanized oil product produced from rapeseed oil treated with sulphur.	10 parts obtained from reacting 93 parts oleic acid and 20 parts zinc benzoate.
c	20 parts sulphur vulcanized soy bean oil	10 parts obtained from reacting 93 parts dehydrated castor oil and 2.8 parts cobalt acetate.
d	20 parts amber colored chlorine-free commercial vulcanized oleo-material.	20 parts obtained from reacting 93 parts oleic acid and 20 parts lead hydroxide.

Example 17

This exemplifies the process of Example 11 as applied to the gels produced in Example 10 from commercial alkyd resins:

	Gel	Contact substance	Added Compound
a	20 parts gel of Example 10*a*	10 parts obtained from 93 parts linseed oil and 1.5 parts cobalt acetate.	2.1 parts bodied non-gelatinized linseed oil.
b	20 parts gel of Example 10*b*	16.5 parts obtained from 93 parts dehydrated castor oil and 2.8 parts cobalt acetate.	3.5 parts dehydrated castor oil.
c	20 parts gel of Example 10*c*	10 parts obtained from 93 parts linseed oil and 1.5 parts cobalt acetate.	2 parts bodied non-gelatinized linseed oil.

The resulting reaction products were thinned with an equal part of toluene and clear stable solutions were obtained. Each of these solutions was mixed with an equal amount of the non-gelatinized starting material and clear stable, soluble products were obtained.

Example 18

The process set forth in Example 11 was modified by adding during, and/or after, the process of liquifying the gel, an amount of natural resins, gums, asphalts, oils and dryers by melting them together.

	Solubilized Reaction Product	Added Compound
a	50 parts solubilized reaction product obtained from process of Example 11 (40 parts linseed oil gel plus 10 parts contact substance from 93 parts linseed oil and 1.5 parts cobalt acetate).	30 parts asphalt.
b	50 parts of solubilized reaction product obtained from process of Example 11 (40 parts linseed oil gel plus 10 parts contact substance from 93 parts linseed oil and 1.5 parts cobalt acetate).	40 parts ester gum, 10 parts lead manganese resinate, 0.5 part cobalt naphthenate dryer.

The final products were thinned with an equal amount of petrol naphtha and formed a stable solution.

Example 19

The process of Example 18 was practiced wherein a phenol-formaldehyde synthetic resinous material was added. The final product was dissolved in an equal volume of toluene and formed a stable solution.

It also has been found that the solubilized final reaction product may be modified by the addition of a gelatinized material and then heating the mixture until gelatinization re-occurs.

Example 20

50 parts of the solubilized final reaction product of Example 11 were heated with 50 parts of China-wood oil to about 300° C. A partially insoluble gelatinized final product was obtained.

Example 20a

The reaction product of each of the foregoing Examples 11–18 inclusive was dissolved in an equal part of toluene. About two parts of ether petroleum were then added to the solution and it was observed that an appreciable portion of gelatinous substance was liberated from the solution.

Example 20b

100 parts of the solubilized final reaction product of Example 11 were slowly heated with 5 parts lamoyl peroxide to a gelatinizing temperature of about 120° C. at which point the product again became an insoluble, gelatinous mass.

Example 21

60 parts solidified alkyd resin (containing about 15 parts polyhydroxyl alcohol, 35 parts phthalic anhydride and 50 parts soy bean oil ingredients) were compounded at a melting temperature of 250° C. with 40 parts reaction product (containing 37% lead) obtained from reacting naphthenic acid and lead acetate.

One part each of the final reaction product produced a clear, stable solution when dissolved in (1) 2 parts non-gelatinized linseed oil; (2) one part toluene; (3) one part mono-styrene; (4) a solution of one part mono-styrene in one part toluene.

In addition, it has been found that the solubilization of the insoluble gelatinized oils may be accomplished with the contact-substances in the presence of other materials such as asphalt, non-gelatinized oils, resins, gums, synthetic resinous materials, such as phenolic resins and alkyd resins.

In accordance with the foregoing examples, it will be understood that the metals of the salts, oxides, peroxides, hydroxides, carbonates, acetates, etc., are not limited to any one group of the periodic system.

It further will be understood that fillers, pigments, etc., may be utilized to modify products of the present invention so that they may be used in the coating and impregnating arts.

It further will be understood that the melting temperature employed to solubilize the insoluble oils by compounding therewith a metal soap-like reaction product is such that substantially the entire mass of the resulting composition is melted into the liquid stage. In this respect the melting temperature of the present invention is distinguished from the use of a lower temperature which is incapable of melting substantially the entire mass into a liquid state. By use of above specified melting temperature it is possible to form a soluble reaction product which is capable of forming a stable solution; whereas this is not possible when a temperature below the melting temperature is employed. Moreover, the solubilized final reaction product, obtained by employing a melting temperature, is capable of being heated without gelatinizing and is further capable of being regelatinized as set forth in Example 20 and 20*a*. Moreover, the regelatinized product may again be solubilized by the process of the present invention.

Coatings, impregnations, coverings, extrusions and compoundings made from the oil base coating compositions of the present invention, possess great elasticity and great resistance to aging, hardening, changes in temperature and humidity and are thereby particularly adapted for the production of coatings, such as varnishes and the like.

The oil base coating compositions of the present invention may be melted with natural or synthetic resins, asphalts, copal gums and the like so as to alter their physical properties, such as to increase hardness, lower elasticity, or for changing color effect, acid resistance, drying conditions and the like. Coatings and impregnations obtained from the oil base coating compositions of the present invention may be further hardened or solidified either during or after drying by the use of vulcanizing or accelerating agents.

In addition, the compositions of the present invention may also be used as plasticizers for resinous compounds, cellulose lacquers, plastic compounds and the like.

Coatings and impregnations made from the oil base coating compositions of the present invention may be dried with or without the application of heat, or drying may be accelerated by the action of polymerization accelerators such as sulphur chlorides, tin tetrachlorides, organic peroxides and the like.

The oil base coating compositions of the present invention may be used for the preparation of oil compounds, varnishes, lacquers, coatings, extrusions, coverings, for the modification of resinous materials, and as impregnations for cloth and the like. In addition, they may be used for producing electrical insulating materials, such as binding materials for fiber windings. They may also be used as heat and moisture insulating materials and as laminating compounds.

I claim:

1. A method of solubilizing an at least partially insoluble and at least partially gelled oil selected from the group consisting of fixed oils and a synthetically produced oil-like ester of a higher fatty acid which comprises melting and compounding with said oil a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acids, higher fatty acid esters, petroleum acids and rosin acids, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble fixed oil reaction product which is capable of forming a stable solution.

2. The process set forth in claim 1, wherein the at least partially insoluble and at least partially gelled oil is derived from a vegetable oil.

3. The process set forth in claim 1, wherein the at least partially insoluble and at least partially gelled oil is derived from an animal oil.

4. The process set forth in claim 1, wherein the at least partially insoluble and at least partially gelled oil is derived from a synthetically produced oil-like ester of a higher fatty acid.

5. A method of solubilizing an at least partially insoluble and at least partially gelled linseed oil which comprises melting and compounding with said oil a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acids, higher fatty acid esters, petroleum acids and rosin acids, at a melting tem-

perature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble linseed oil reaction product which is capable of forming a stable solution.

6. A method of solubilizing an at least partially insoluble and at least partially gelled China-wood oil which comprises melting and compounding with said oil a compound comprising a metal soap of a compound selected from the ground consisting of higher fatty acids, higher fatty acid esters, petroleum acids and rosin acids, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble China-wood oil reaction product which is capable of forming a stable solution.

7. A method of solubilizing an at least partially insoluble and at least partially gelled soy bean oil which comprises melting and compounding with said oil a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acids, higher fatty acid esters, petroleum acids and rosin acids, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble soy bean oil reaction product which is capable of forming a stable solution.

8. A method of solubilizing an at least partially insoluble and at least partially gelled composition comprising a synthetically produced oil-like ester of a higher fatty acid and a polyhydric alcohol having not more than 6 OH groups, which comprises melting and compounding with said composition a compound selected from the group consisting of higher fatty acids, higher fatty acid esters, petroleum acids and rosin acids, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble reaction product which is capable of forming a stable solution.

9. A method of solubilizing an at least partially insoluble and at least partially gelled composition comprising a synthetically produced oil-like ester of a higher fatty acid and a polyhydric alcohol having not more than 6 OH groups and an ester-forming acid, which comprises melting and compounding with said composition a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acids, higher fatty acid esters, petroleum acids and rosin acids at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble reaction product which is capable of forming a stable solution.

10. A method of solubilizing an at least partially insoluble and at least partially gelled composition comprising a synthetically produced oil-like ester of a higher fatty acid and a polyhydric alcohol having not more than 6 OH groups and phthalic anhydride, which comprises melting and compounding said composition, a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acids, higher fatty acid esters, petroleum acids and rosin acids at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble reaction product which is capable of forming a stable solution.

11. A method of solubilizing an at least partially insoluble and at least partially gelled oil selected from the group consisting of fixed oils and a synthetically produced oil-like ester of a higher fatty acid which comprises melting and compounding with said oil a compound comprising a metal soap of a higher fatty acid substance, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble fixed oil reaction product which is capable of forming a stable solution.

12. A method of solublizing an at least partially insoluble and at least partially gelled oil selected from the group consisting of fixed oils and a synthetically produced oil-like ester of a higher fatty acid which comprises melting and compounding with said oil a compound comprising a metal soap of a petroleum acid, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble fixed oil reaction product which is capable of forming a stable solution.

13. A method of solubilizing an at least partially insoluble and at least partially gelled oil selected from the group consisting of fixed oils and a synthetically produced oil-like ester of a higher fatty acid which comprises melting and compounding with said oil a compound comprising a metal soap of a higher fatty acid ester, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble fixed oil reaction product which is capable of forming a stable solution.

14. A method of solubilizing an at least partially insoluble and at least partially gelled oil selected from the group consisting of fixed oils and a synthetically produced oil-like ester of a higher fatty acid which comprises melting and compounding with said oil a compound comprising a metal soap of a naphthenic acid, at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage, whereby to form a soluble fixed oil reaction product which is capable of forming a stable solution.

15. A soluble, stable oil composition comprising the reaction product of an at least partially insoluble and at least partially gelled oil selected from the group consisting of fixed oils and a synthetically produced oil-like ester of a higher fatty acid with a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acids, higher fatty acid

esters, petroleum acids and rosin acids compounded at a melting temperature below the decomposition temperature of the resulting composition and at such melting temperature that substantially the entire mass of the resulting composition is melted into the liquid stage.

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REFERENCES CITED

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

FOREIGN PATENTS

Number	Country	Date
1,386	Great Britain	1901