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METHOD FOR SOLUBILIZING AT LEAST PARTIALLY INSOLUBLE AND GELATINIZED WAXES

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This invention relates to the solubilizing of insoluble and gelatinized, or at least partially insoluble or partially gelatinized, wax-type esters as they are generally known in the art; that is, higher fatty acid esters of high atomic polyhydroxyl alcohols having less than three OH groups.

This invention further relates to the solubilizing of at least partially insoluble or at least partially gelatinized oil-type esters; that is, higher fatty acid esters of polyhydroxyl alcohols having more than two OH groups.

The present application is a continuation-in-part of my pending allowed United States application Serial No. 748,665, now matured into Patent No. 2,476,879, wherein I have disclosed and claimed a method of solubilizing an at least partially insoluble and at least partially gelled oil selected from the group consisting of fixed oils and synthetically produced oil-like esters 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. This application, Serial No. 748,665 is in turn a continuation-in-part of my abandoned application Serial No. 496,262.

Reference is hereby made to my pending application Serial No. 33,676, wherein I have disclosed and claimed a method of insolubilizing and solidifying fatty acid esters of alcohols which comprises treating said esters with a potentially, free oxygen-yielding compound incapable of forming a metal soap with said esters, at a temperature sufficiently elevated to effect release of said free oxygen in said esters whereby to form a solidified composition which is insoluble in coal tar and petroleum solvents. Thus in the latter application, Serial No. 33,676, I have disclosed that the formation of an at least partially insoluble state is not limited to the polyhydroxyl alcohol fatty acid esters (having more than two OH groups) of the type disclosed in Serial No. 748,665, but I have additionally disclosed a process for at least partially solidifying such products which are derived from alcohols having less than 3 hydroxyl groups.

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Thus the present application presents a process for solubilizing and utilizing the esters of polyhydroxyl alcohols having less than three hydroxyl groups. More specifically, the present application is primarily concerned with the solubilization of a class of natural and synthetic substances known as waxes. It is difficult to specifically define a wax because of the range of products to which the term is applied, although for present purposes the waxes may be regarded as consisting chiefly of higher fatty acid esters of mono- and dihydroxy high atomic alcohols, associated with one or more of the free fat and wax acids, free monohydric alcohols and sterols, hydrocarbons, and lactones or other condensation compounds. See "The Chemistry and Technology of Waxes" by Warth, 1947.

Thus, wax-forming esters such as cetyl palmitate are regarded as waxes. Waxes are generally referred to as being of insect, vegetable, animal, semi-mineral or mineral origin. The waxes of mineral origin are known as unsaponifiable waxes which consist largely of hydrocarbons; e. g., ozokerite and ceresin. The mineral waxes and paraffin waxes consist of a group of hydrocarbons related to methane and are therefore not properly definable as waxes in that they do not consist primarily of higher fatty acid esters of mono- or dihydric high atomic alcohols and higher fatty acids.

In contrast to these unsaponifiable hydrocarbon mineral waxes, the waxes generally known as semi-mineral waxes comprise mostly esters of high molecular weight alcohols and acids, plus free acids. Accordingly, the semi-mineral waxes, such as montan wax, are more properly classifiable as natural vegetable type waxes such as carnauba or candelilla type waxes which are incompletely saponified with alkali (see page 6 of the booklet "Waxes" by American Cyanamid and Chemical Corp.). Accordingly, semi-mineral waxes of the montan type come within the purview of the present invention; whereas, mineral and paraffin waxes do not come within the purview of the present invention.

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 increased 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. For example, waxes which can be readily transformed as by polymerization, or by the application of heat, by distillation or by chemical action into a partially insoluble condition and having some swelling ability, are generally used in a non-gelatinous condition. Thus gelatinized waxes 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 waxes, 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 at least partially insoluble, gelatinous, swollen waxes 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 wax base composition having a high shrinkage capacity when dried from a state of solution.

A further object of the invention is to provide a process for solubilizing a swelled, at least partially insoluble, gelatinous wax base composition.

Still another object of the invention is to provide a process for modifying the coating characteristics of waxes so as to bring then 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 wax 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, natural or synthetic fixed oils of the type disclosed in my aforesaid application Serial No. 748,665, and the like.

Still another object of the invention is to provide a process for solubilizing gelatinized wax 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 waxes 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 wax 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 wax 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 waxes, 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 the metal soap-like reaction products, preferably formed by reacting a wax, fixed oil, fatty acid, a petroleum acid, a rosin acid, or mixture thereof with a compound of a metal capable of reaction with such waxes, oils, fatty acids, rosin acids, naphthenic acids or other organic compounds to form a corresponding wax soluble metal soap-like reaction product can be used to solubilize and influence the degree of swelling of waxes 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 waxes 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 wax 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 and which is in a liquid state at the melting temperature of the above set forth process.

According to my invention, waxes, 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 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 wax which may be 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 waxes which are film-forming but also those solidifications 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 wax or fixed oil.

By stable I mean to include any compound or solution which will remain in a balanced condi-

tion 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, waxes, 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 material 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 waxes, 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 waxes 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 waxes 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 wax and the contact substance depends in part upon the degree of swelling of the insoluble, gelatinized wax. If the gelatinized wax 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 wax is in a condition which may not be readily swelled. Thus, it has been found that fresh gelatinized waxes require a smaller proportion of contact substance than is required for gelatinized waxes which are in an aged condition. Likewise, certain waxes, which have been highly gelatinized by continued heating, distillation or vacuum treatment, require an increased amount of contact substance. Waxes 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, wax 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 liquefying proceeds parallel with the forming of metal sulphides which can be removed subsequently from the liquefaction.

For purposes of clarity, the various natural and synthetic fatty acid esters of polyhydroxyl alcohols having three or more hydroxyl groups will be referred to as the oil-type esters, whereas the various natural and synthetic fatty acids esters of polyhydroxyl alcohols having less than three hydroxyl groups will be referred to as the wax-type esters.

Thus, certain of the following examples relate to a preferred process for the preparation of a metallic soap-like contact substance by compounding natural or synthetic materials of the wax-type or natural or synthetic materials of the oil type, or both, with metal soap-forming metals, metal oxides, or metal salts, which resultant reactions products are used as a contact substance for solubilizing an at least partially insoluble gelatinized wax-type material. Additionally, the wax-type contact substance may be used for the solubilization of at least partially insoluble, gelatinized oil-type materials. Thus, the foregoing objects should be understood to cover the solubilization of natural or synthetic oils which are in an at least partially gelled and in at least partially insoluble state by heating and compounding therewith a metal soap of a wax-type substance.

Example 1

The following examples illustrate the use of materials of the wax-type for preparation of the metal soap-like contact substance for insolubilizing and solubilizing purposes.

(*a*) 50 parts of carnuba wax, a natural plant wax, were heated with ten parts of chromium carbonate at about 100° C. and above, the carbonic acid gas escaped under foaming. Heating was continued until the reaction slowed down, which in this instance occurred at about 270° C. Upon cooling the reaction product appeared as a solid greenish substance. This contact substance was subsequently used for solubilization as illustrated in subsequent examples.

(*b*) 50 parts of shellac wax, a natural animal wax, were heated with ten parts red lead oxide. Heating was continued until reaction ocurred at about 100° C. Heating was then continued up to 250° C. and a metal soap-like contact substance was obtained, which upon cooling to room temperature apeared as a dark brown solid material.

(*c*) 50 parts of montan wax, a natural lignite wax, also referred to as a semi-mineral wax, were heated with 12 parts zinc formate which

were added to the wax melt at around 110° C. Foaming occurred up to about 160° C., at which temperature the foaming subsided somewhat. Heating was continued with the occurrence of strong foam formation around 235° C. Heating was slowly continued up to about 275° C. Upon cooling to room temperature, a metal soap-like contact substance was obtained.

(*d*) In a modification of Example 1(*c*) above, 60 parts of montan wax were heated in a similar manner with 20 parts lithium carbonate and heating was continued up to around 270° C., at which point the contact substance was obtained.

(*e*) 31 parts of polyethylene glycol-di-tri-ricinoleate, a synthetic wax-type substance, were heated with 5 parts of cobalt acetate. Strong foaming developed around 100° C. and at around 150° C., a bluish liquid state was obtained and a slight wax-like form was observed in the area where the compound was in contact with the relatively cool air of the room. Heating was continued at around 200° C., the film was no longer observed and a uniform melt of brownish shade was obtained. Heating was continued somewhere slightly beyond 220° C. at which stage a semi-solid contact substance was obtained upon cooling.

(*f*) In a similar manner, 45 parts candelilla wax were heated with 5 parts chromium carbonate. Foaming was most evident between 95 and 125° C., heating being continued up to around 280° C. The reaction product had an appearance similar to the product of Example *a* and was used subsequently for liquefying solid waxes and oils.

(*g*) 42 parts ouricuri wax were heated with 10 parts nickel sulphate and the reaction was carried up to about 280° C. A dark brown colored reaction product was obtained and used in a later example for the liquefying process.

(*h*) 58 parts of Japan wax were heated with 5 parts lithium hydroxide. After a quickly beginning foam formation, the heating was carried gradually up to around 275° C. Since some unreacted substance was observed, the melt was filtered through cheesecloth and a clear liquid was obtained which later hardened in cooling. The product was used as a contact substance in a later example for liquefying solid oil and wax.

(*i*) 39 parts of Japan wax were reacted in heating with 6 parts of silver nitrate. The reaction occurred around 220° C. The product remained cloudy, and was used in later examples as a contact substance.

(*j*) 20 parts Japan wax were heated with 6 parts aluminum sulfate. A liquid was formed initially and thereafter the natural wax portion of the compounded mixture combined with the aluminum salt to form a solid reaction product which remained solid up to 250° C. The remainder of the compounded mixture formed a liquid metal salt product which was then separated from the solid matter by filtration. Upon cooling, the liquid portion became a soft wax-like material which was subsequently used as a contact substance in the succeeding examples disclosing actual liquefaction.

(*k*) 20 parts of Japan wax were reacted under heating with 5 parts cupric oxalate. Heating was continued under occasional stirring up to and above 245° C. A greenish cloudy product was obtained which was used in a following example as a contact substance in liquefying at least partially insoluble substances.

(*l*) 27 parts of beeswax were reacted with 4.5 parts bismuth benzoate by heating and compounding for about 30 minutes up to around 250° C. A light yellowish brown reaction product was obtained.

(*m*) 25 parts beeswax were heated and reacted with 5 parts manganese oxalate, heating being continued up to about 270° C. A medium brown reaction product was obtained.

(*n*) 20 parts ouricuri wax were heated and reacted with 6 parts zinc benzoate upon heating up to around 255° C. A reddish dark brown product was obtained.

(*o*) 18 parts carnauba wax were heated and compounded with 3 parts basic aluminum acetate up to about 280° C. A brownish wax-like product was obtained.

(*p*) 30 parts polyethylen-glycol di-tri-ricinoleate, a synthetic wax-type composition were heated and reacted with 5 parts chromium oxalate. A brownish compound was formed under foaming during the heating which was continued up to around 275° C.

(*q*) 12 parts carnauba wax were heated and reacted with 2 parts magnesium carbonate and under foaming, a brownish compound was obtained. The heating was continued up to around 255° C.

(*r*) 5 parts candelilla wax were mixed with 15 parts China-wood oil and the mixture was heated and reacted with 4 parts magnesium carbonate up to 255° C. The reddish brown product was subsequently used as a contact substance.

(*s*) 17 parts of beeswax were reacted with 3 parts antimony trioxide under gradual heating and stirring up to about 270° C. A greyish brown contact substance was obtained.

(*t*) 42 parts liquid polyethylene glycol 400 di-tri-ricinoleate were heated and compounded with 7 parts zinc formate. Heating was carried to about 260° C.

(*u*) 15 parts ouricuri wax were heated and reacted with 3 parts aluminum borate. Very strong foaming was observed initially but the reaction subsided and heating was discontinued around 270° C.

(*v*) 25 parts diethylene glycol monolaureate, a synthetic wax type composition, was heated with 5 parts cobalt acetate up to about 240° C. for about 15 minutes.

Example 2

The following examples illustrate the utilization of the wax-type reaction products as formed by the methods set forth in the preceding examples, either alone or in a mixture with minor amounts of oil-type reaction products as disclosed in the aforementioned application S. N. 748,665, for the solubilization of at least partially insoluble oil-type materials.

(*a*) This example discloses the solubilization of a natural oil gel with a contact substance derived from a natural wax made in accordance with the preceding example:

20 parts of gelatinized linseed oil, which was at least partially insoluble and incapable of forming a stable solution with solvents such as petroleum naphtha or coal tar solvents, were heated with ten parts of the carnauba wax-type contact substance set forth in the preceding Example 1(*a*). Heating was continued to about 200° C. at which point a liquefied appearance was noticed. Heating was continued under stirring up to a temperature of 270° C. At this point, and the point of cooling, the resulting

composition was capable of being completely dissolved in the usual solvents. Thus, in this instance, 1 part of the resulting composition was substantially completely dissolved in 1.5 parts of toluene. The dissolved solution was then filtered and stored. Following several days' storage, the solution was further diluted with 2 additional parts toluene and subsequently with 2 parts VMP petroleum naphtha, thereby illustrating that other solvents can be used for the solution of the resulting composition. It is desired to point out that the aforementioned solvents are normally used for dissolving ungelatinized natural oils.

(*b*) This example illustrates the liquefaction or solubilization of a gelatinized natural oil by melting and compounding therewith a contact substance derived from a synthetic wax product.

40 parts of gelatinized soybean oil were heated with 20 parts of polyethylene glycol-di-triricinoleate contact substance as formed in the preceding Example 1(*c*). The melting and compounding was carried out as in Example 2(*a*) above until liquefaction and solubilization was obtained at around 215° C. and thereafter heating was continued to about 270° C. After cooling, the resultant composition was dissolved in a ratio of one part to two parts of toluene and a stable liquefaction was obtained in the form of a true solution.

(*c*) This example illustrates the solubilization of a solid natural oil with a natural wax contact substance in the presence of a soluble oil.

Ten parts of solid linseed oil prepared (in accordance with the method described and claimed in my co-pending application Ser. No. 33,676) by treatment with a potentially, free, oxygen-yielding compound incapable of forming a metal soap, at a temperature sufficiently elevated to effect the release of the free oxygen; in this instance benzoyl peroxide. The resultant solidified linseed oil was insoluble in coal tar and petroleum solvents. The ten parts solid linseed oil were heated with 5 parts of a shellac wax-type contact substance prepared in accordance with Example 1(*b*) above in the presence of 10 parts of soluble bodied linseed oil known commercially as type Z–2. The soluble oil was added as a wetting agent in order to increase the effect of the contact substance on the dry solid linseed oil. The mixture was compounded and heated until liquefaction occurred at around 250° to 265° C. The product was then thinned in a one to one ratio with petroleum naphtha and was further diluted by adding one part toluene to 5 parts of the naphtha solution. A stable soluble solution resulted. It will be apparent that the liquefaction may be accelerated by reducing the particle size of the solid linseed oil, as by breaking up the initial solid material into small chunks and particles.

(*d*) This example illustrates the liquefaction of an at least partially insoluble gel of a synthetic oil with a wax-type contact substance. 12 parts gelled dehydrated castor oil, known commercially as "Castung oil 103," were heated and compounded with 5 parts of the contact substance produced in Example 1(*c*) above from a synthetic wax. Liquefaction was reached at about 240° C. and the compound was further heated to about 265° C. and was thereafter dissolved in a one to one ratio with a xylene solvent.

(*e*) A similar effect as in the preceding example was obtained from gelled dehydrated castor oil by heating and compounding 10 parts of this gel with two parts of a natural lignite wax-type contact substance as produced in Example 1(*c*). Liquefaction was obtained at around 240° C. and heating was continued to about 270° C. The resulting composition was dissolved in about 20 parts of a hydrated solvent known commercially as "Dekalin."

(*f*) This example illustrates the liquefaction of a solid modified polyhydroxyl alcohol fatty acid and phthalic anhydride ester, which may be identified as a solidified at least partially insoluble alkyd resin. 20 parts of a solid alkyd resin prepared by solidifying a commercial non-drying type oil-modified alkyd resin known commercially as "Rezyl 92–5" by a compounding heat treatment with benzoyl peroxide, were heated with 10 parts of montan wax type substance as prepared in Example 1(*c*) above. The compounding and heating was performed in the presence of 6 parts soybean oil, liquefication being obtained around 235° C., and heating continued up to around 280° C. The resulting composition was completely dissolved in equal parts toluene.

(*g*) This example illustrates the liquefaction of an at least partially insoluble oil gel with a mixture of contact substances, one being derived from an oil and the other being derived from a wax.

50 parts gelatinized perilla oil were liquefied by heating and compounding with a mixture of 5 parts contact substance obtained by reacting 93 parts linseed oil and 5 parts lead acetate together with 3 parts of the wax-type contact substance of Example 1(*a*) above. Liquefaction was obtained at around 225° C. and heating was continued at around 275° C. The product was substantially completely dissolved in about 1½ parts benzol.

(*h*) 12 parts heat-gelled linseed oil, which was partially insoluble and incapable of forming a stable solution with solvents, were resolubilized by heating and compounding with 4 parts of the contact substance obtained from Japan wax and aluminum sulfate as described in preceding Example 1(*j*). The liquefied substance obtained at around 270° C. was of a relatively light color. It was completely diluted with 20 parts toluene. An application on a steel panel produced a resistant and glossy coating on baking at 105° C. for 45 minutes.

(*i*) 18 parts of a gelled dehydrated castor oil, which was partially insoluble and incapable of forming a stable solution, were reliquefied by heating and compounding with 10 parts of the metal soap-like reaction product produced in preceding Example 1(*k*) from Japan wax and cupric oxalate. Liquefaction was obtained at around 260° C. and the product was completely thinned with 20 parts tetra-hydro-naphthalene (Tetralin).

(*j*) In a manner similar to Example *c*, 10 parts solid linseed oil as described in Example *c* above, were liquefied by heating with 7 parts of a contact substance comprising the reaction product as derived from Example 1(*h*), by heating and compounding 58 parts of Japan wax as in Example *c* with 5 parts lithium hydroxide. Liquefaction was obtained around 280° C. and heating was continued up to 300° C. The product was completely thinned in 20 parts toluene.

(*k*) In a similar manner, 15 parts solid linseed

oil were liquefied by heating and compounding with 25 parts of the metal soap-like reaction product of Japan wax and silver nitrate described in Example 1(*i*). Liquefaction was obtained at around 260° C. and heating was continued up to 300° C. The product was uniformly thinned in a 1:1 ratio in toluene.

(*l*) In a similar manner, 10 parts of solid olive oil, produced by reacting olive oil with 9% t-butyl perbenzoate in the method as described in Example *c*, were liquefied by heating and compounding with the metal soap-like reaction product obtained from heating candelilla wax with chromium carbonate (see Example 1(*f*)).

(*m*) 10 parts solid cod-liver oil, produced by heating and compounding twice with 7% di-tertiary-butyl-diperphthalate, were liquefied by heating and compounding with 8 parts of the metal soap-like reaction product of Example 1(*g*), (heating ouricuri wax with nickel sulfate). The liquefaction proceeded as described above in Example *j*.

(*n*) 3.5 parts of an insoluble substance, obtained from China-wood oil by mixing it with about 0.5% anhydrous ferric chloride and holding it at around 50° C. for 24 hours, were reliquefied by heating and compounding with 8 parts of a contact substance prepared from ouricuri wax and zinc benzoate as set forth in Example 1. 3 parts of a second type of commercial iron naphthenate (6% Fe) was added to the mixture as an additional metal soap-like contact substance. By heating the mixture under stirring for 2 hours up to around 280–295° C. a dark melt was obtained which was dissolved in 15 parts tetrahydronaphthalene (Tetralin). This solution was applied to a bonderized steel panel and dried over night in an oven at around 100° C. A coherent dry coating was obtained which had a Sward hardness of around 17.

(*o*) 16 parts of gelled linseed oil, which was at least partially insoluble in varnish solvents, like toluene, were reliquefied by heating with 8 parts of a greyish brown contact substance obtained from reacting up to around 270° C. 17 parts of beeswax with 3 parts of antimony trioxide. The liquefaction of the gelled oil with this contact substance was completed at around 265° C. and the product was thinned with toluene in the proportion of 1:1. A greenish solution was obtained which on cooling had a slightly cloudy appearance.

(*p*) 9 parts of at least partially insoluble and gelled solid linseed oil obtained in accordance with Example 1 were reliquefied by heating with 6 parts of a wax-type contact substance in the presence of 4 parts heat-break-stabilized linseed oil. The wax-type contact substance was prepared by heating 12 parts carnauba wax with 2 parts magnesium carbonate up to about 245° C. The liquefaction was completed at around 290° C. and the fused substance was thinned with 20 parts of a hydrated solvent, tetrahydronaphthalene.

(*q*) 12 parts of gelled linseed oil were reliquefied by fusing together (up to around 275° C.) with 7 parts of a wax-type contact substance at around 275° C. The liquefaction was thinned with equal parts toluene. The wax-type substance was prepared by heating and reacting 27 parts beeswax with 4.5 parts bismuth benzoate heating being continued up to around 250° C. A light yellowish brown substance was obtained which served as a contact substance in this example.

(*r*) 10 parts synthetic oil, commercial sorbitol-soybean-fatty acid-ester oil, which had been at least partially insolubilized by heating and compounding with a free oxygen releasing catalyst (see Example 1), and which had been freed from its soluble oil components by heating with benzol followed by drying, were reliquefied by heating to about 280–285° C. with 5 parts of a wax-type contact substance. The wax-type contact substance was produced by heating up to 270° C. and reacting 25 parts beeswax with 5 parts manganese oxalate. As a wetting agent, 1.5 parts of a liquid synthetic was polyethylene glycol-400-di-tri-ricinoleate were added to the mixture during compound heating. The resulting liquefaction was diluted with solvent naphtha in the proportion of 1 part non-volatile substance with 1.5 parts volatile matter.

(*s*) This example illustrates reliquefying a joint insolubilization or solidification product obtained from reacting 26 g. linseed oil (type bodied oil Z–2) and 52 g. monostyrene under heating with 7 g. of a free oxygen releasing catalyst, t-butyl perbenzoate. The reaction was observed at around 145° C. and 51.5 g. solids were obtained. These solids would not dissolve in hot toluene, they would not form a coherent film, and did not melt when put on the heated surface of a conventional covered laboratory electric hot plate. On heating 5 parts of these solids with 11 parts of a contact substance prepared from 30 parts polyethylene glycol-400-di-tri-ricinoleate and 5 parts chromium oxalate by heating and compounding from 200 to around 275° C., the linseed oil-styrene solids were reliquefied. The product was soluble in equal parts toluene. In applying the solution to a steel plate and drying it around 100° C. over night, a coherent film formation was obtained. Liquefaction occurred upon heating at 250° C. for about 70 minutes and stopping the heating at 270° C.

(*t*) 8 parts heat-gelled long-oil alkyd gel, prepared by heating 18 parts of a commercial long-oil alkyd (Glyptal 2475), in an open vessel at around 280–300° C. until a strong gel had been formed, were liquefied by heating and reacting with 14 parts of a metal soap-like contact substance prepared by heating 42 parts polyethylene glycol 400 di-tri-ricinoleate with 7 parts zinc formiate. Liquefaction of the gel was accomplished at around 270° C. The product was readily dissolved in equal parts benzol.

(*u*) 11 parts of a partially solidified, partially gelled and at least partially insoluble long-oil alkyd product was prepared by heat reacting a long-oil plastic alkyd (Aroplaz 1085) in the presence of 5–10% t-butyl hydroperoxide. The product was liquefied by heating with 14 parts of the contact substance used in the previous example. The product was liquefied around 260° C. and was readily soluble in VMP petroleum naphtha.

(*v*) 15 parts of the same at least partially insoluble long-oil alkyd were liquefied by heating and compounding with 6 parts of the contact substance prepared as in Example 1 by heating 25 parts of beeswax with 5 parts manganese oxalate up to about 270° C. Liquefaction was accomplished at around 250° C. and was completed around 265–275° C. The product was dissolved in equal parts toluene.

(*w*) 15 parts of solidified, incoherent substance which was at least partially insoluble in varnish solvents like benzol, petroleum solvents, hydrated solvents, etc., was produced by heat-

reacting a short oil-modified alkyd resin (in this case commercial Rezylresin 310–5), in the presence of 7% t-butyl-perbenzoate. The solidification was solubilized after moistening with 10 parts volatile toluene and heating and compounding with 8 parts of the contact substance prepared by heat-reacting 15 parts ouricuri wax with 3 parts aluminum borate as set forth in Example 1. Liquefaction was completed around 280° C. and the product was dissolved in equal parts tetrahydronaphthalene (Tetralin).

(*x*) 16 parts of gelled and at least partially insoluble linseed oil were resolubilized by heating and compounding with 10 parts of a contact substance produced from 25 parts di-ethylene glycol monolaureate, a synthetic wax type composition, and 5 parts cobalt acetate as in Example 1(*v*). The resolubilization occurred at around 260° C. and heating was continued up to about 275° C. The product was completely dissolved in 20 parts solvent naphtha.

Example 3

The following examples illustrate the resolubilization of at least partially insolubilized waxes and gelled wax derivates by means of contact substances derived from natural and synthetic oils in accordance with the aforementioned application S. N. 748,665.

(*a*) 10 parts of partially insolubilized carnauba wax, a natural plant wax, were liquefied by heating and compounding with ten parts of a contact substance obtained by compounding 93 parts linseed oil with 1.5 parts cobalt acetate at a temperature somewhat above 200° C. The carnauba wax and the linseed oil type contact substance were heated and compounded, liquefaction occurring at around 240° C. Heating was continued up to about 280° C. and the product was thereafter dissolved in two parts VMP petroleum naphtha, thereby resulting in a stable state of solution. The resulting solution was applied to a bonderized steel panel, dried by baking at 120° C. for 45 minutes and then aged for 24 hours at 50° C. A dry film coating was obtained on the steel panel.

In another application, 55 parts of the product solution was combined with 48 parts of a paste consisting of 20 parts lead formate, 10 parts red lead, 4 parts zinc oxide, 11 parts linseed oil (type Z–2) and 3 parts VMP petroleum naphtha. The resulting paint compound was applied to a steel panel and baked and aged as in the case of the preceding example. The resulting film had a Sward hardness of 6.

(*b*) 10 parts of at least partially insoluble animal wax; namely, spermaceti wax, were liquefied by heating and compounding with 10 parts of a contact substance obtained by melting and compounding 50 parts of a sorbitol-soybean fatty acid ester with 4 parts manganese carbonate at about 200° C. The partially solidified spermaceti wax and the contact substance were heated and compounded to about 220° C. until the reaction subsided and a uniform liquid was obtained. The resulting composition was substantially completely dissolved in equal parts benzol.

(*c*) 10 parts of at least partially insolubilized montan wax, a natural lignite wax, were liquefied by heating and compounding with 6 parts of linseed oil type contact substance as used in Example 3(*a*) above. In order to increase the wetting capacity of the contact substance on the solidified montan wax, 10 parts toluene were added. As heating was continued the solvent evaporated, but was not replaced since it was only initially of benefit in increasing the wetting capacity of the catalyst on the solidified montan wax. Liquefaction was obtained at around 270° C. and heating was continued up to around 290° C. The resulting composition was diluted with 15 parts xylene.

(*d*) 16 parts of an at least partially insolubilized synthetic wax; namely, polyethylene glycol-di-tri-ricinoleate, was resolubilized by heating and compounding with an oil-type contact substance obtained by compounding and heating 90 parts of linseed oil and 2 parts iron oxide, as set forth in the aforementioned co-pending application S. N. 748,665. The insoluble synthetic wax and the contact substance were heated and compounded up to a temperature of about 240° C. at which time liquefaction was obtained. Heating was continued to 280° C. and the resulting composition was then thinned with 2 parts toluene.

(*e*) 10 parts partially insoluble beeswax were liquefied by heating and compounding with 9 parts of a contact substance obtained from reacting 93 parts of soybean oil with 6 parts lead acetate at about 240° C. The compounds were heated under stirring to about 250° C. whereupon uniform liquid state was observed. Heating was continued to about 270° C. and the product uniformly thinned with a mixture of 10 parts solvent naphtha and 10 parts toluene.

(*f*) 10 parts partially insoluble carnauba wax were liquefied after moisting with 10 parts of a volatile solvent, in this case xylene, by heating and compounding with 8.5 parts of a contact substance (obtained from reacting 40 parts soybean oil with 6 parts nickel sulfate gradually up to 250° C. and above). In the liquefaction process, the liquid state was observed at around 260° C. Heating was continued up to 290° C. and the product was uniformly thinned with 20 parts toluene.

(*g*) 10 parts of at least partially insoluble solvent purified Japan wax were reliquefied by heating with 20 parts of a contact substance obtained from heating 30 parts of dehydrated castor oil with 9 parts zinc formiate up to around 250 to 260° C. whereby a light yellowish brown product was obtained. The mixture of the wax and the prepared contact substance was heated to around 285° C. under stirring. The liquefied reaction product was completely dissolved in 50 parts xylene and a true solution was obtained.

(*h*) 8 parts of partially insoluble carnauba wax, which had been purified three times by boiling with toluene followed by drying at 100° C. for 3 days, were reliquefied by heating and compounding them up to 310° C. with 10 parts of a greenish colored contact substance obtained by heating 25 parts commercial lard oil (X–298) with 6 parts copper oxalate up to around 280° C. The liquefaction of the carnauba wax was completely dissolved in 25 parts benzol.

(*i*) Beeswax, obtained from reacting 50 parts crude beeswax under heating with 9 parts t-butyl perbenzoate and purified by heating with 500 parts toluene and by filtering off the undissolved at least partially insoluble solid wax from the toluene solution and dried over night at 100° C., was used in this example. The treated beeswax does not melt at temperatures up to about 300° C. But it was made fusible by heating and compounding up to 240° C., 6 parts of this wax with 10 parts of a contact substance derived from heating 10 parts of teaseed oil with

3.5 parts lithium mono-hydroxide. Under very strong foaming, a reddish brown compound was formed which remained liquid under heating and was decanted from a small residue of unliquefied crystalline substance. The resulting contact substance and the prepared beeswax were heated under stirring up to 295° C. and formed a fused, liquid compound.

In a similar manner, 6 parts of the same prepared beeswax were fused into a liquid state by heating with 15 parts of another contact substance derived from heating 20 parts soybean oil with 5 parts silver nitrate up to around 290° C. The contact substance was dark and cloudy in appearance.

(*j*) 8 parts of at least partially insoluble carnauba wax were fused and liquefied by heating and compounding with 10 parts of a contact substance obtained from heating 26 parts soybean oil with 5 parts antimony oxide up to 280° C. A slightly yellow liquefaction was obtained.

(*k*) 10 parts of at least partially insoluble beeswax were liquefied by heating with 13 parts of a contact substance obtained from heating and compounding 23 parts cod-liver oil with 4 parts bismuth benzoate up to about 260° C. This contact substance was a dark brown material which showed some sedimentation of unreacted bismuth benzoate. Liquefaction was obtained on heating the prepared wax and the contact substance up to 295° C. under stirring. The resulting solution in equal parts xylene appeared as a greenish brown compound.

(*l*) 4 parts at least partially insoluble ouricuri wax were liquefied by heating and compounding with 6 parts of a contact substance obtained from heating 20 parts menhaden fish oil with 4.5 parts chromic acetate up to around 255° C. This contact substance had a blueish brown color and showed that some unused surplus of metal salt remained undissolved. The wax was liquefied with this contact substance on heating and compounding at around 275–285° C. The resulting liquefaction was dissolved in equal parts benzol.

(*m*) 10 parts of the same contact substance as in the preceding example were used for liquefying 8 parts at least partially solidified polyethylene glycol-di-tri-ricinoleate. The liquefaction was obtained at around 270° C. The product was thinned with equal parts xylene to form a true solution.

(*n*) 8 parts at least partially insoluble beeswax were liquefied by heating with 12 parts of a contact substance obtained from heating and compounding 20 parts cottonseed oil with a slight excess (3 parts) of aluminum hydroxide. At around 265° C., a light colored oil was decanted and used for the liquefaction of the wax. Liquefaction was completed at around 285° C. and a 1:1 toluene solution was made up, which was light colored and wax-like in appearance after cooling.

(*o*) 9 parts of an at least partially insoluble ouricuri wax were reliquefied by heating and compounding with 10 parts of a contact substance produced by reacting 12 parts of a synthetic commercial oil ("Neo Fat 17") based on C_{22} acids, with 2 parts magnesium carbonate. The reaction subsided around 260° C. after strong foaming and on cooling, the reaction product was a solid wax-like material. In the liquefying process, heating and compounding was carried up to about 290° C. A dark solution was obtained which was diluted with two parts hydrated solvent (Tetralin).

(*p*) 5 parts at least partially insoluble polyethylene glycol-di-tri-ricinoleate were liquefied by using a metal soap-like contact substance derived from a synthetic fatty acid-ester of a resinous polyhydroxyl alcohol (the commercial esterification of dehydrated castor oil with Epon resin, which is a resinous polyhydroxyl alcohol). 45 parts of this synthetic oil-type ester were heated with 10 parts manganeous oxalate up to 275–280° C. A very tough and light colored product was obtained, which was used as the contact substance: 5 parts of the treated synthetic wax-like substance, 8 parts of the contact substance and 5 parts of the initial liquid synthetic wax-like substance, the latter being added as a wetting agent, were heated and compounded up to about 280° C. A liquefied, uniform product was obtained which was dissolved in equal parts xylene. The resulting solution produced a coherent film when baked onto a steel panel.

(*q*) 12 parts at least partially insoluble ouricuri wax, obtained by reacting ouricuri wax with about 8–11% t-butyl perbenzoate under heating and compounding up to around 175° C. and followed by solvent extraction of the residual soluble matter with benzol, were solubilized by heating and compounding with 16 parts contact substance produced from beeswax and manganese oxalate as described in Example 1. Liquefaction was obtained at around 280° C. and the product was readily dissolved in equal parts toluene.

(*r*) 7 parts of the same ouricuri wax were liquefied by heating with 7 parts of a contact substance produced from ouricuri wax and zinc benzoate according to Example 1. The liquefaction was performed up to around 285° C. and the product was directly dissolved in one and one-half parts xylene.

(*s*) 8 parts of the same ouricuri wax were liquefied by heating up to about 255° C. with 8 parts of a wax-type contact substance. The contact substance was obtained by heating and reacting 18 parts carnauba wax with 3 parts basic aluminum acetate as described in Example 1. The liquefaction was thinned with equal parts xylene. After cooling, the solution had a soft wax-like appearance.

(*t*) 8 parts of an at least partially solidified polyethylene glycol-400-di-tri-ricinoleate were moistened with 4 parts toluene and then compounded and heated up to 265° C. for about 40 minutes with 9 parts of a wax derived contact substance. This contact substance was produced from heating and reacting 18 parts carnauba wax with 3 parts aluminum acetate up to about 280° C. At room-temperature it appeared as a wax-like coherent solid. The liquefaction of the solids was diluted with a hydrated solvent (comercial Hexalin) in the proportion of 1 part non-volatile to 1 part volatile substance. On cooling, a slightly waxy solution was obtained.

(*u*) 10 parts at least partially insoluble ouricuri wax were liquefied by heating up to about 260° C. and reacting with 10 parts of a contact substance produced from heating 17 parts beeswax with 3 parts antimony trioxide up to about 270° C. The resulting liquefaction was thinned with equal parts benzol and was further diluted with the same amount of VMP naphtha.

(*v*) 5.5 parts of the same ouricuri wax were liquefied by heating and reacting with 7 parts of a contact substance (under Example 1) produced from heating a mixture of candelilla wax and China-wood oil with magnesium carbonate, as in Example 1. The liquefaction was produced in the presence of 1.5 parts of soybean oil under

heating up to about 265° C. The compound was readily dissolved in one and one-half parts xylene.

(*w*) 10 parts of the same ouricuri wax were liquefied by heating and compounding with 8 parts of a contact substance produced by heating and reacting beeswax with manganese oxalate. The liquefaction was complete at around 280° C. and was readily dissolved equal parts in benzol.

(*x*) 6 parts of at least partially solidified wool fat, a wax-type animal product, were liquefied by heating with 11 parts of a contact substance produced from heating and reacting 12 parts carnauba wax with 2 parts magnesium carbonate. To increase the initial contact between the two substances, 6 parts of a volatile solvent (xylene) were added. Heating and compounding were continued up to about 270–280° C. and the product was thinned with solvent naphtha in the proportion of 1 part non-volatile matter with 2 parts solvent.

(*y*) 10 parts of solidified and at least partially insoluble polyethylene glycol-400-di-tri-ricinoleate were liquefied by heating with 9 parts of a contact substance (produced under Example 1 from the same material in its liquid soluble state and chromium oxalate). The wetting of the solids was facilitated by adding at the start 3 parts volatile solvent (xylene) and the liquefaction was completed at around 250° C. The product was readily dissolved in equal parts toluene.

(*z*) The preceding example was repeated with a contact substance produced from the reaction product of 57 parts of the liquid synthetic wax with 10 parts bismuth benzoate, and similar results were obtained.

(*aa*) 3.5 parts at least partially insoluble beeswax, as used in earlier examples, were solubilized by heating and compounding in the presence of 1 part liquid soybean oil with 7 parts of a contact substance. This contact substance was produced by heating and reacting 20 parts of a polyhydroxyl alcohol fatty acid phthalic acid-ester compound, that is an oil-modified alkyd (commercial Rezyl 310–5), with 3 parts aluminum borate until foaming subsided at around 255° C. A light brown reaction product was obtained.

(*bb*) 3.5 parts of the same beeswax was liquefied in the presence of 1 part soybean oil by heating and compounding with 7 parts of said contact substance until liquefaction was obtained at around 250° C. The product was thinned with 1.4 parts hydrated solvent (commercial Hexalin).

(*cc*) 10 parts of a solidified polyethylene glycol-400-di-tri-ricinoleate were liquefied with 10 parts of a contact substance produced from a long-oil-modified alkyd (commercial Glyptal 2475), by reacting and compounding 15 parts thereof with 2.5 parts chromium carbonate up to 270–280° C. The liquefaction of the solid synthetic wax was completed around 255° C., heating being continued up to 280° C. The product was dissolved in equal parts benzol. A light colored solution was obtained.

(*dd*) 8 parts treated ouricuri wax, as used in previous examples, were liquefied by heating and reacting with 8 parts of a contact substance prepared from a plastic-type, long-oil modified alkyd (commercial Aroplaz 1085 plastic). The contact substance was prepared by heating and compounding 54 parts of this alkyd with 10 parts lead acetate up to 260° C. and a light brownish product was obtained which was of a resin-like appearance at room temperature. Liquefaction of the wax was completed around 270° C. and the product was readily dissolved in equal parts VMP petroleum solvent.

Example 4

The following examples exemplify the resolubilization of at least partially insoluble waxes by heating and compounding therewith contact substances of the wax-type prepared in accordance with Example 1 above.

(a) 10 parts of an at least partially insolubilized spermaceti wax, a natural wax, was used in the crude form in which it contained a gelled, partially solidified portion. The contact substance used in this instance was of the shellac wax type prepared in accordance with Example 1(*b*) above. To intensify the solubilizing reaction, 10 parts of a wetting substance, in this instance, a synthetic oil, namely, synthetic sorbitol-linseed fatty acid esterification product, known commercially as "Atlas oil G 875" was used. Liquefaction was obtained at around 250° C. The resulting composition was thinned with 1.5 parts toluene solvent.

(*b*) 50 parts of at least partially solidified insoluble natural wax, spermaceti wax in this instance, was resolubilized with 70 parts of a contact substance produced from a synthetic wax in accordance with Example 1, above. In this instance, the contact substance comprised a metal soap formed from polyethylene glycol-di-tri-ricinoleate and cobalt acetate. Liquefaction of the solidified spermaceti wax with the synthetic contact substance was obtained at about 200° C. and the resulting composition was thinned with a two-part compounded solvent consisting of half xylene and half petroleum naphtha.

(*c*) 20 parts of solidified and at least partially insoluble montan wax were resolubilized by heating and compounding with 10 parts of a contact substance produced as set forth in Example 1(*c*), in this instance, a montan wax type contact substance. The heating and compounding was continued under stirring up to about 300° C. at which time liquefaction occurred. The resulting composition was thinned with 40 parts benzol solvent. A clear solution was obtained which upon application to a metal surface in the form of a steel panel gave a flat and uniform coating upon drying. In a similar test with a cobalt metal soap contact substance of the montan wax type, a finished film coating on a steel panel was exposed to mineral oil (Shell grade Diala oil #15) and heated to between 90 and 100° C. It was observed that the film was not attacked by the oil up to this temperature.

(*d*) 20 parts of an at least partially insolubilized synthetic wax, in this instance, diethylene glycol mono-laureate (known commercially as "Glaurin" (were liquefied by compounding and heating with 20 parts of a contact substance derived from shellac wax and red lead oxide as set forth in Example 1(*b*) above. The liquefaction was carried out in the presence of 10 parts of diethyleneglycol mono-laureate utilized as a wetting agent for increasing the contact between the solid and the contact substance. Liquefaction occurred at about 250° C. The resulting composition was thinned by adding 2.2 parts of toluene solvent, the solvent being added after the liquefaction had been cooled to about the boiling temperature of the solvent.

(*e*) This example exemplifies the liquefaction of an at least partially insoluble synthetic wax with a contact substance derived from a synthetic wax.

20 parts of solidified di-ethylene glycol monolaureate were liquefied by heating and compounding with 20 parts of a contact substance prepared in accordance with Example 1(*e*) above, in this instance, the reaction product of a poly-ethylene glycol-di-tri-ricinoleate and cobalt acetate. The solidified synthetic wax and the synthetic wax type contact substance were heated and compounded up to about 270° C. at which point the liquefaction was observed. The resulting composition was thinned in an equal amount of toluene solvent.

(*f*) This example exemplifies the liquefaction of an at least partially insoluble wax by utilization of mixture contact substances derived from an oil.

10 parts of insolubilized carnauba wax were resolubilized by heating and compounding with a mixture of 12 parts of contact substance obtained from the reaction product of 93 parts linseed oil and 2.5 parts iron oxide plus 6 parts of contact substance in the form of a reaction product obtained from 60 parts beeswax with 5 parts basic bismuth acetate, the latter having been prepared in accordance with Example 1(*b*) above. The liquefaction of the insoluble carnauba wax with the mixture of contact substances, consisting of both an oil type and a wax type, was accomplished at around 225° C. Heating was continued to about 250° C. and the resulting composition was diluted with 40 parts xylene solvent.

(*g*) 21 parts partially insolubilized Japan wax were liquefied by heating and compounding with 17 parts of a metal soap-like reaction product which has been produced by heating 58 parts Japan wax with 5 parts lithium hydroxide (Example 1(*h*)). Liquefaction occurred at around 250° C. and heating was continued to around 290° C. Upon cooling the product was completely diluted with 40 parts benzol.

(*h*) 10 parts partially solidified beeswax were resolubilized by heating and compounding with a contact substance comprising 4 parts of the reaction product of the Example 1(*g*) (curicuri wax and nickel sulfate) and 3 parts of the reaction product from Example 1(*f*) (candelilla wax and chromium carbonate). The solubilizing reaction was completed around 280° C. and the product was uniformly thinned with 20 parts of xylene.

(*i*) In another test, 10 parts solidified, partially insoluble montan wax were reliquefied by heating and compounding with 9 parts of a metal soap-like reaction product obtained from heating 39 parts of Japan wax with 6 parts silver nitrate (Example 1(*i*)). Liquefaction was observed around 245° C. Heating was continued to around 280° C. and the product was thinned in a 1:1 ratio with toluene.

(*j*) 15 parts of the solidified and at least partially insoluble montan wax were reliquefied by heating them with 12 parts of the metal soap-like reaction product of Example 1(*f*) (which consisted in reacting 45 parts of candelilla wax with 5 parts chromium carbonate). Liquefaction was obtained around and above 275° C. The product was diluted with 30 parts of the hydrated solvent, namely a commercial Hexaline.

(*k*) 12 parts partially insolubilized synthetic wax, in this instance polyethylene glycol di-tri-ricinoleate, were liquefied by heating and compounding with 10 parts of a contact substance comprising the reaction product produced in Example 1(*j*) from Japan wax and aluminium sulfate. The liquefaction was obtained at around 255° C., and heating was continued to about 275° C. The product was uniformly thinned with 20 parts of xylene.

(*l*) 10 parts of an at least partially solidified diethylene glycol monolaureate were liquified by heating and compounding with 8 parts of a contact substance produced from 25 parts diethylene glycol monolaureate, a synthetic wax type composition, and 5 parts cobalt acetate as in Example 1(*v*). Liquefaction was obtained after heating up to about 255° C. and the product was completely thinned with equal parts benzol.

Example 5

The following examples exemplify the resolubilization of at least partially insoluble waxes by means of contact substances of the free acid type.

(*a*) In exemplifying the use of a fatty acid, 6 parts solidified beeswax in its crude form were resolubilized by treatment with 3 parts fatty acid contact substance; namely, a commercial copper oleate. Liquefaction of the solidified beeswax with the fatty acid contact substance occurred around 220° C. The product was dissolved in 10 parts tetrahydronaphthalene. On cooling the product to room temperature, it thickened to a wax-like form, but was readily dissolved upon slight warming by thinning with about 10 additional parts solvent.

(*b*) 5 parts solidified diglycol stearate, recovered after a solvent purification, were resolubilized with 10 parts commercial lead naphthenate containing about 24% lead. 4 parts of a volatile VMP naphtha which evaporated during the liquefaction heating were used as a wetting substance. The liquefaction was obtained at about 240° C. The product was dissolved in 15 parts of toluene and remained liquid at room temperature.

(*c*) In this example, a naphthenate type substance, commercial cobalt naphthenate containing about 6% cobalt was used as a contact substance. 15 parts solidified, at least partially insoluble American montan wax was obtained by heating 54 parts thereof with a free-oxygen releasing catalyst comprising 7 parts tertiary butyl perbenzoate until solidification occurred at about 260° C. The 15 grams solid montan wax was heated and compounded with 13 parts of the cobalt naphthenate substance in addition to 7 grams mineral spirits being added as a volatile solvent wetting agent. The mineral spirits evaporated during heating and reaction was observed at about 130° C. Heating was continued and at around 230° C. all the solid montan wax appeared to have been solidified. Heating under stirring was continued to about 250° C. The resulting composition was dissolved in 60 parts benzol and the solution thereof was applied on a steel panel in the form of a film which was baked at about 100° C., whereby a permanent film of considerable gloss was obtained.

In a similar example, solidified montan wax was liquefied with a montan wax type contact substance and a film was prepared on a steel panel as in the preceding example. The film was tested for its resistance to mineral oil (Shell grade Diala oil 15 being used). It was noted that the film was not attacked by the oil until the temperature exceeded 115° C., thus illustrating the film-forming characteristics of the resolubilized wax formed in accordance with the

present process from initially solid and insoluble wax.

(*d*) In this instance a rosin acid type contact substance was utilized, the contact substance being prepared from rosin acid and manganese acetate to give a manganese resinate. 5 parts of at least partially insolubilized shellac wax were reliquefied by heating with 5 parts manganese resinate in the presence of 2.5 parts linseed oil used as a wetting substance. Liquefaction was obtained at about 230° C. and the product was dissolved in 20 parts xylene solvent.

(*e*) In this instance, a nickel resinate contact substance was utilized. 5 parts of at least partially insolubilized solid carnauba wax in its crude form were resolubilized by heating with a mixture of 3.5 parts nickel resinate contact substance plus 1.5 parts of a shellac wax-red lead contact substance as obtained in Example 1(*b*) above. The solid carnauba wax and the mixture of the nickel resinate and shellac wax contact substances were heated and compounded in the presence of 2 parts corn oil used as a wetting substance. Liquefaction occurred around 245° C. and the product was dissolved in 15 parts toluene solvent.

(*f*) 2.8 parts solidified carnauba wax were resolubilized by heating with 20 parts of a solution consisting of 10 parts of calcium naphthenate (4% calcium) contact substance in 10 parts of VMP naphtha. The solvent used as a wetting substance evaporated during the heating and at about 225° C. liquefaction was obtained. The reaction product was dissolved in 10 parts toluene.

(*g*) In another test, the liquefaction product of a solidified montan wax, obtained by treatment with cobalt naphthenate, was thinned with toluene in a 1:1 ratio and this solution was further diluted with 3 times the amount of a ketone solvent, in this case methyl-iso-butyl-ketone, which is a preferred solvent for various groups of coating materials. A clear solution was obtained which remained stable during 2 weeks' storage at room temperature.

In another test, 5 parts solidified montan wax was mixed with 20 parts solid linseed oil as described in Example 2 (c), and this mixture was liquefied by heating and compounding with 30 parts of a commercial naphthenate, in this case lead naphthenate (24% lead). Again the reaction product was thinned with 25 parts toluene. Afterwards the resulting solution was further diluted with 40 parts methyl-iso-butyl ketone and a stable, clear solution was obtained.

(*h*) 5 parts of solidified and at least partially insoluble beeswax were moistened with 2 parts toluene. As a contact substance, a mixture of 5 parts commercial calcium naphthenate solution (5% Ca) and 7 parts commercial zinc naphthenate solution (8% Zn) were added. The compound was heated up to about 275° C. for about 45 minutes and a fused mass was obtained. This mass was dissolved in 20 parts tricresylphosphate. On cooling, a soft, waxy soluble substance was obtained.

(*i*) 18 parts of at least partially solidified and insolubilized and non-fusable beeswax were liquefied by heating and compounding with 7 parts non-volatile cobalt octoic metal soap contact substance and 13 parts volatile matter. To facilitate the wetting 7 parts of toluene were added. In this instance, commercial cobalt octoic drier (6% Co) and obtained in a solution with 35% nonvolatile matter was used. Liquefaction of the solids was observed at around 275° C. and heating was discontinued at around 295° C. The product was dissolved in 25 parts toluene and a clear blue solution was obtained. This solution was clearly miscible in equal parts methyl-iso-butyl ketone. It was also clearly miscible with equal parts monostyrene.

(*j*) 16 parts gelled linseed oil were heated with 5.5 parts non-volatile cobalt-octoic acid product in the presence of 10 parts volatile matter. The melting product was held between 275 and 290° C. for about 30 minutes until complete liquefaction had been obtained. The resulting product was readily diluted with equal parts toluene. The liquefied wax from the preceding example was mixed in equal parts with this solution of the liquefied oil gel and clear solutions were obtained.

Example 6

The following examples exemplify the resolubilization of a mixture of at least partially insoluble waxes and at least partially insoluble oils.

2.5 parts of a solidified wax substance, namely, polyethylene glycol-di-tri-ricinoleate were added to 3.5 parts of a solidified oil product, namely, solidified sorbitol-linseed fatty acid ester (known in the commercial form as Atlas oil G-375). The mixture of the oil and wax insoluble substances were solubilized by heating and compounding with 6.9 parts of a contact substance consisting of a mixture of 5.5 parts lithium naphthenate and 1.4 parts manganese naphthenate (6% Mn). The liquefaction was accomplished in the presence of 1.5 parts soluble oil; in this instance, the soluble sorbitol-linseed fatty acid ester was used. The liquefaction was obtained at about 230° C. The product was dissolved in a mixture of 6 parts coal tar solvent, namely, toluene, and 10 parts hydrated solvent, namely deka-hydronaphthalene.

Example 7

In order to exemplify the addition of pigments, colors, etc., in order to modify the process and products of the present invention, for use in the coating and impregnating arts, the solubilized product obtained in Example 3(*a*), namely, soluble carnauba wax, was pigmented with a pigment compound consisting of a mixture of 35 parts lead chromate, 17 parts red lead and 8 parts zinc oxide. This pigment was ground into the soluble carnauba wax until a normal paint consistency was obtained and additional amounts of naphtha were added to enable the application of a uniform coating. The resulting paint composition was applied to panels which were dried for 45 minutes at 120° C. and a dry uniform coating was obtained.

In accordance with the present invention it has been found that the solubilization of at least partially soluble gelatinized natural or synthetic waxes or natural or synthetic oils, or combinations thereof, may be accomplished with wax-type or oil-type contact substances, or both, in the presence of other materials such as asphalts, non-gelatinized oils, non-gelatinized waxes, resins, gums, synthetic resinous materials, such as phenolic resins, alkyd resins and the like. It will also be understood that the final products of the present invention may be supplemented or modified by the addition of other oleo or resinous compounds, pigments, etc., for improving their application and use in the coating and impregnating arts. Thus, the physical properties, such as hardness, elasticity, color affinity, acid re-

sistance, drying conditions and the like may be improved by the aforementioned additions. In addition, the resulting compositions of the present invention may be hardened or solidified by the addition of vulcanizing or accelerating agents. Additionally, the compositions of the present invention may also be used as plasticizers for resinous compounds, lacquers such as cellulose lacquers, plastic compounds and the like.

It will be understood that the melting temperatures utilized to compound and solubilize the insoluble wax-type compounds or the insoluble oil-type compounds, or both, with either the oil-type or the wax-type contact substance, or both, is of such degree that substantially the entire mass of the resulting composition is melted into the liquid state without resulting in any decomposition. This melting temperature, as will be observed by reference to the foregoing examples, is generally in the neighborhood of 200° C. or above. In this respect, the required melting temperature is to be distinguished from the use of a lower temperature which is incapable of melting substantially the entire mass into a liquid state, or a higher temperature which would result in decomposition. Thus by virtue of the present invention, it is possible to form a soluble resulting composition which is capable of forming a stable solution, and one which is capable of being further diluted with the usual coal tar and petroleum solvents. Moreover, the solubilized final product is capable of being heated without gelatinization and is further capable of being regelatinized into a gel or other solid forms by utilization of a free-oxygen releasing catalyst in the manner described in my pending application Ser. No. 33,676. Additionally, it should be pointed out that the resulting regelatinized and resolidified product resulting from reaction with a free-oxygen yielding catalyst may again be solubilized by means of the process of the present invention.

The present process has the further advantage that natural and synthetic wax compositions and natural and synthetic oil compositions may be decolorized and purified; that is, they may be freed of undesirable components in the solid state and in an at least partially solid state and can thereafter be resolubilized in accordance with the present invention for use in the coating and impregnating arts.

A further advantage resulting from the present invention is that liquefactions of the insoluble wax or oil compounds can be produced which are in the form of soluble solids at room temperatures prior to dilution or thinning with the usual solvents. Thus, these soluble solids can be kept easily, stored and shipped in a soluble solid form and can thereafter readily be dissolved in solvents and diluted for use in the arts.

Still another advantage of the present invention is that since the solubilized wax type or oil type products can be liquified in such manner that their melting point is considerably higher than that of the original soluble waxes and oils as commercially obtained in the natural synthetic state, and since such melting point can be modified by altering the ratio of the insoluble oil or wax to the contact substance, and further by adding varying amounts of preferred components as heretofore mentioned, it is thereby possible to produce impregnating and insulating compounds, paper coating and fabric treating compounds of a greater stability and usefulness than can be obtained from the use of the original oil or wax compounds as they exist initially in their natural or synthetically produced state.

A still further advantage of the present invention is that the at least partially insoluble or solidified oil or wax compounds may be separated from such soluble components as are contained therein, such as by solvent extraction, and it is therefore possible by the present invention to produce solubilized and liquified products which are practically free from such additional compounds which make them incompatible with other waxes, oils or resins. In this manner it is possible to produce clear and soluble solutions which are free from undesired materials.

The wax or oil base compositions of the present invention may be used for the preparation of varnishes, lacquers, coatings, extrusions, coverings, modifiers for resinous materials, impregnations for cloth and the like. They may also be used for producing electrical insulating materials, such as binding materials for fiber bindings, in addition to being used for heat and moisture insulating materials and as laminating compounds.

I claim:

1. A method of solubilizing an at least partially insoluble higher fatty acid ester of an alcohol having from one to two hydroxy groups which comprises melting and compounding with said ester a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acid esters of a polyhydric alcohol, higher fatty acids, 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 compostiion is melted into the liquid stage, whereby to form a soluble ester reaction product capable of forming a stable solution.

2. The method set forth in claim 1 wherein the at least partially insoluble higher fatty acid ester comprises such an ester of a dihydric alcohol.

3. The method set forth in claim 1 wherein the at least partially insoluble higher fatty acid ester comprises such an ester of a mono-hydric alcohol.

4. The method set forth in claim 1 wherein the at least partially insoluble higher fatty acid ester comprises a synthetically produced wax-like ester of a higher fatty acid.

5. A method of solubilizing an at least partially insoluble natural wax which comprises melting and compounding with said wax a compound comprising a metal soap of a compound selected from the group consisting of higher fatty acid esters of a polyhydric alcohol, higher fatty acids, 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 wax reaction product capable of forming a stable solution.

6. The method set forth in claim 5 wherein the at least partially insoluble natural wax comprises an animal wax.

7. The method set forth in claim 5 wherein the at least partially insoluble natural wax comprises a vegetable wax.

8. The method set forth in claim 5 wherein the at least partially insoluble natural wax comprises an insect wax.

9. A method of solubilizing an at least partially insoluble wax which comprises melting and

compounding with said wax a compound comprising a metal soap of an oil selected from the group consisting of fixed oils and synthetically produced oils containing 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 wax reaction product capable of forming a stable solution.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,476,879	Kronstein	July 16, 1949