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PROCESS OF BODYING DRYING OILS AND
THE PRODUCT RESULTING THEREFROM

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This application is in part a continuation of an application Serial No. 435,080 filed by applicants Henry G. Berger, George S. Crandall and John F. Socolofsky on March 17, 1942.

This invention is concerned with novel methods for the preparation of varnishes and other bodied drying oil products and with the novel compositions of matter produced by the technique herein disclosed. More particularly, the invention relates to incorporation of preformed drying oil gels in drying oils and the like.

Heretofore, varnishes and the like of high quality, have been prepared almost exclusively from a relatively few drying oils, primarily the "hard" oils such as China-wood oil and perilla oil. These oils may be bodied readily, and dry to form superior films. China-wood oil, perilla oil and others have, however, been difficult to obtain and under the most favorable commercial circumstances expensive and are, due to war conditions, now rapidly approaching a state of exhaustion insofar as this country is concerned. "Synthetic substitutes" have been proposed. For example, it is possible to dehydrate castor oil to produce conjugated diolefins. Another type of alternative is exemplified by saponification of relatively cheap oils such as fish oils, separation of free acids by fractional distillation and re-esterification of selected cuts.

We have now developed a quick-bodying oil at least as valuable as China-wood oil for formation of films, using oils readily available from sources in continental United States and South America. Our novel oil is not only superior to any of the synthetic substitutes known to us, such as dehydrated castor oil, re-esterified selected oils of free acids from saponified fish oils, etc., but also it is the equal of or superior to any of the previously used film protecting oils including the expensive and scarce China-wood

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oil. Not only is it possible by our process to save economically by using relatively cheaper and more abundant drying oils such as oiticica and dehydrated castor oils to produce equally good or improved varnish substitutes in place of more expensive and scarce oils such as China-wood oil, but it also is possible to save economically by using a small quantity of such oils from which to form a gel, and then dispersing this gel in an even much cheaper and more abundant oil such as linseed oil, soyabean oil or fish oils to form a highly satisfactory varnish. Moreover, it is possible with great success to gel catalytically a mixture of two or more oils such as, for example, oiticica oil and dehydrated castor oil, oiticica oil and linseed oil, or oiticica oil, dehydrated castor oil and linseed oil, and to disperse this gelled mixture in one of the quick-drying or semi-drying oils such as, for example, linseed oil. Whereas prior art practices have stressed avoidance of gel formation during the cooking of drying oils to the desired body, we have found that superior results are obtained by incorporating a preformed gel derived from certain drying oil with the oil to be bodied. By this expedient, we avoid the precautionary measures necessary to prevent gelation of the oil being bodied and allow the use of temperatures and/or cooking times which would have a deleterious effect on the drying and film-forming properties of the finished product if it were made by conventional methods from quick-drying oils such as oiticica, perilla and dehydrated castor oils or even from China-wood oil.

According to our process, the main body of the oil is not polymerized to the stage at which it has the desired body for the final product. Instead, either another oil or a portion of the oil to be used is subjected to extensive polymerization to form a gel which is then dispersed in

the unbodied oil to form a quick-drying oil. The gel for incorporation in the oil to be bodied may be prepared from China-wood oil by thermal treatment. A better product, however, may be obtained if the gel is prepared from certain other quick-drying and semi-drying oils or from a combination of two or more of them as later to be described by catalysis. Where a catalyst is used, a polymerization catalyst, such as boron fluoride or hydrogen fluoride is uniformly mixed with the raw oil and the mass reacted at moderate temperature until the whole is converted to a gel.

We prefer the use of boron fluoride and hydrogen fluoride as catalysts. Other polymerization catalysts such as metallic halides can be used but, since according to our process the catalyst remains in the final varnish, these metallic salts are undesirable because they adversely affect the varnish film. Excessive amounts of catalyst cause the reaction to proceed too rapidly and may impair the quality of the gel. In general we prefer to use amounts in the range of 0.01 to 1.0% by weight of catalyst. It is recommended that boron fluoride be used in amounts of about 0.1%.

The gel resembles the "art gum" of commerce in many respects, is translucent in relatively thin layers and shows a characteristic gel-type fracture. The mass of gel is broken into small pieces, preferably finely divided as by passing through a roller mill. The milled product strongly resembles the crumbs obtained by erasing with art gum and has a relatively high capacity to absorb oxygen. This latter property renders it desirable to use the milled product promptly since it tends to become hard and less soluble in drying oils after taking up oxygen. It may also take up oxygen so rapidly as to burst into flame and precaution against fire must be taken if the milled gel is stored.

While satisfactory varnishes may be made according to our process by gelling any one or a combination of two or more of many quick-drying, slower drying, or semi-drying oils and then dispersing the gels so formed in an unbodied oil, by far the better products are obtained by catalytic gelation of one or more oils selected from the class consisting of oiticica oil, perilla oil and dehydrated castor oil. We have been unable to disperse gels formed by catalysis from China-wood oil by any means known to us. Anomalous, China-wood oil may be gelled by heat and then dispersed but the varnishes formed from dispersion of thermally gelled China-wood oil are not as good as varnishes formed from catalytically gelled oiticica, perilla or dehydrated castor oil. Specifically, the drying time of varnishes so formed from China-wood oil is slow and the resistance of the dried film to attack by water and caustic is poorer than that of our preferred varnishes. On the other hand, we have been unable to obtain satisfactory dispersions of any thermally gelled drying or semi-drying oils excepting China-wood oils. For example dispersion of minor amounts of heat gelled oiticica oil was attempted by the use of a Waring Blendor and though a uniform mixture seemed to have been obtained after a considerable time, yet when the product was flowed out tiny particles of gel were discernible. Furthermore the slower drying oils such as linseed oil, soyabean oil, fish oils, etc., even when they can be gelled catalytically and dispersed yield inferior products. However, as stated, such slower drying oils such as for example linseed oil may be mixed with the preferred

oils (i. e., with oiticica, perilla and dehydrated castor oils) before gelation and the mixture gelled and then dispersed in an unbodied oil to form a superior varnish. In such cases the slower drying oil should be a minor component (i. e., less than 50%). Also two or more of the preferred oils (oiticica, perilla and dehydrated castor) may be mixed with each other before gelation. Such mixture may also have a minor amount of linseed oil added before gelation.

After the formation of such a gel, according to the next step of our preferred process, the gel is added to and uniformly dispersed in a mass of untreated drying oil or semi-drying oil. In order to secure the best results in this step we prefer that the mixture be heated until the gel is thoroughly dispersed. Prepared in this manner, the oil may be employed in any of the known uses for bodying oils, as for example, conversion to varnish by cooking with suitable resins. It is also feasible to add resins before the step of heating to disperse the gel and thus complete the varnish-making in one step.

The gels formed by catalytically gelling oiticica, perilla, and dehydrated castor oils or mixtures thereof (such as a mixture of one or more of these oils with linseed oil in which the linseed oil is less than 50% of the mixture) may be dispersed in any of the quick-drying, slow drying, semi-drying oils, and in some of the non-drying oils. For example, unbodied tung oil, oiticica oil, perilla oil, dehydrated castor oil, linseed oil, soyabean oil, poppy oil and fish oils may be used. However, we prefer to disperse the gel in one of the drying or semi-drying oils such as unbodied tung oil, oiticica oil, perilla oil, dehydrated castor oil, linseed oil and soyabean oil. However, if unbodied tung oil is used, a gelation inhibitor (e. g. sulfur) must be used in order to obtain a satisfactory dispersion.

The dispersion may be obtained by stirring finely divided particles of the gel into the raw oil and heating the mixture to a temperature of at least about 500° F. A dispersing agent may be used as is described below and if so the gel need not be ground or need not be ground so finely. If the gel is finely ground and no dispersing agent is used we prefer temperatures of about 560° to 580° F. during a relatively short time.

Our process finds particular application in the preparation of bodied oils and varnishes from the slower drying oils and semi-drying oils such as linseed oil and soyabean oil. The advantages of a process which permits the replacement of an active drying oil (e. g. perilla oil) in whole or in part by a less active and more readily available oil are obvious. We have prepared ester gum varnishes from our products, which compare very favorably with a commercial tung oil-ester gum varnish prepared by conventional means. Typical results are shown in a table set out hereinafter. It is notable that ester gum varnishes made from mixtures of linseed oil and oiticica oil (ungelled) are not satisfactory varnishes. (See Example IV below.)

We have used dispersion agents to assist the dispersion of the gel in the oil in some of our tests. However, in general, we have found them to be unnecessary if the gel is properly prepared and is ground sufficiently fine. In general, as stated above, temperatures on the order of 560° to 580° F. during a relatively short period are desirable to give satisfactory compositions without the use of dispersing agents when the gel is finely ground. When a dispersing agent is used,

lower temperatures of about 520° F. to 550° F. are sufficient, and milling of the gel is unnecessary since small lumps may be readily dispersed.

During the step of heating the mixture of gel and unbodied oil to produce a bodied oil composition, it is noted that heat is apparently evolved during the latter part of the cooking operation. We have prepared varnish bases using cooking periods of 45 minutes to 3 hours at various temperatures and noted clear evidence of exothermic reaction about 20 minutes before the end of that operation regardless of total cooking time. The dispersion may or may not involve a chemical reaction (such as for example a bodying of the unbodied oil in which the gel is dispersed), but such a reaction is a distinct possibility. We do not believe that the fact of whether there is bodying of the unbodied oil can be definitely established since there are other factors affecting the viscosity of the mixture during the process of dispersing.

EXAMPLE I

Oiticica oil was gelled by the addition of 0.1% boron fluoride and heating for 5 to 10 minutes. This product is a solid resembling art gum. A mixture of 50 parts of this gel and 150 parts of raw linseed oil were mixed in a Waring Blender. To this gel-oil mixture was added 100 parts ester gum and 0.4 part of isoquinoline. This entire charge (50 parts oiticica gel, 150 parts linseed oil, 100 parts ester gum and 0.4 part isoquinoline) was then heated with stirring for 95 minutes at 560° F. This varnish base was cooled to 400° F. and thinned by the addition of 450 parts petroleum thinner and driers containing 1.5 parts lead, 0.105 parts manganese and 0.15 parts cobalt. The resulting varnish had a body C— (Gardner-Holdt) at 40% non-volatile, and dried dust-free in 1¼ hours, tack free in 4½ hours, and hard overnight. The film was of normal hardness and had good water resistance.

EXAMPLE II

Oiticica oil gel was prepared as in Example I. The gel was then ground on a roller mill. This form of the gel is referred to as "milled" gel. Linseed oil 100 parts, ester gum 100 parts and "milled" oiticica oil gel 100 parts were heated with stirring for 135 minutes at 560° F. This varnish base was then cooled to 400° F. and to it was added 352 parts of petroleum thinner and driers containing 1.5 parts lead, 0.105 part manganese and 0.15 part cobalt. The resulting varnish had a body of C (Gardner-Holdt) at 46% non-volatile, and dried dust-free in 1¼ hours, tack free in 5 hours, and hard overnight. The film was of normal hardness and had good water resistance.

EXAMPLE III

Milled oiticica gel (prepared as in Example II) 20 parts, ester gum 100 parts and linseed oil 180 parts were heated with agitation for 210 minutes at 530° F. This varnish base was then cooled to 400° F. and to it was added 157 parts of petroleum thinner and driers containing 1 part lead, 0.70 part manganese and 0.1 part cobalt. The resulting varnish had a body of B— (Gardner-Holdt) at 56% non-volatile, and dried dust-free in 2 hours, tack free in 6 hours, and hard overnight. Film hardness was normal, water resistance good and the varnish was non-reactive in zinc test.

EXAMPLE IV

A varnish consisting of linseed oil 180 parts, oiticica oil 20 parts and ester gum 100 parts was prepared by conventional cooking means with a cooking time of 240 minutes at 590° F. The varnish base was reduced to 55% non-volatile with thinners and driers to contain 1 part lead, 0.70 part manganese and 0.1 part cobalt. This varnish had a body of B+ and required 2½ hours to become dust free and was not tack free in 4 days.

EXAMPLE V

Linseed oil 170 parts, (milled) catalytically gelled dehydrated castor oil 30 parts (prepared by the procedure of Example I) and 100 parts ester gum were heated at 560° F. for 155 minutes. The varnish base was cooled to 400° F. and to it was added 300 parts petroleum thinners and driers containing 0.6 part lead, 0.04 part manganese and 0.04 part cobalt. The resulting varnish had a body of C (Gardner-Holdt) at 50% non-volatile, and dried dust-free in 2½ hours, tack-free in 8 hours, and hard overnight. The film was of normal hardness and had good water resistance.

EXAMPLE VI

Catalytically gelled tung oil was insoluble at all temperatures in linseed oil, soyabean oil, fish oil, etc. The presence of a resin or of various dispersion agents was of no value.

EXAMPLE VII

Heat gelled oiticica oil was, likewise, insoluble.

EXAMPLE VIII

Soyabean oil 100 parts, "milled" oiticica gel (prepared according to Example I) 100 parts, and ester gum 100 parts were heated at 550° F. for 145 minutes. The varnish base was cooled to 400° F. and to it was added 300 parts petroleum thinners and driers containing 1.5 parts lead, 0.105 part manganese, and 0.15 part cobalt. The resulting varnish had a body of D (Gardner-Holdt) at 50% non-volatile, and dried dust-free in 1¼ hours, tack-free in 5¾ hours and hard overnight. The film was of normal hardness and had good water resistance.

EXAMPLE IX

Oiticica oil 100 parts, "milled" oiticica gel 100 parts (prepared according to Example I), ester gum 100 parts, and isoquinoline 0.6 part were heated at 580° F. for 10 minutes. The varnish base was cooled to 400° F. and to it was added 300 parts petroleum thinners and driers containing 1.5 parts lead, 0.105 part manganese, and 0.15 part cobalt. The resulting varnish had a body of D (Gardner-Holdt) at 50% non-volatile, and dried dust-free in ¼ hour, tack-free in 3½ hours, and hard in 8 hours. The film was of normal hardness and had excellent water resistance.

The above examples are exemplary only as will be readily understood by those skilled in the art. Gels derived from various drying and semi-drying oils may be dispersed in drying and semi-drying oils of the same or different nature to produce superior bodied drying oil compositions. The relative proportions of gel and unbodied oil may be varied widely, depending upon the type of product desired.

We include herewith a table of atmospheric exposure tests comparing ester gum varnishes prepared according to our procedure with previously known commercial varnishes as indicated.

TABLE I
Atmospheric exposure tests

Description of Varnish		Condition After Exposure For—			
		6 Wks.	9 Wks.	13 Wks.	17 Wks.
<i>Conventional Type Varnishes</i>					
Heat Bodied Oiticica Oil Ester Gum (25 gal.)		Failed			
Commercial 25 gal. China-Wood Oil—Ester Gum Varnish		O. K.	Failed		
Commercial 25 gal. China-Wood Oil—Perilla Oil—Bakelite Varnish		O. K.	O. K.	O. K.	Failing.
Commercial 25 gal. China-Wood Oil—Bakelite Varnish		O. K.	O. K.	O. K.	O. K.
<i>New Type Varnishes—Using Gel of Example I</i>					
Oil Composition	Resin				
Oiticica Gel, 100 parts; Oiticica Oil, 100 parts.	Ester Gum, 100 parts.	O. K.	Failed		
Oiticica Gel, 100 parts; Linseed Oil, 100 parts.	Ester Gum, 100 parts.	O. K.	O. K.	Failed	
Oiticica Gel, 100 parts; Soyabean Oil, 100 parts.	Ester Gum, 100 parts.	O. K.	O. K.	do.	
Oiticica Gel, 50 parts; Linseed Oil, 150 parts.	Ester Gum, 100 parts.	O. K.	O. K.	O. K.	O. K.
Oiticica Gel, 100 parts; Linseed Oil, 200 parts.	Ester Gum, 100 parts.	O. K.	O. K.	O. K.	O. K.
Oiticica Gel, 100 parts; Soyabean Oil 100 parts.	Bakelite, 100 parts.	O. K.	O. K.	O. K.	O. K.

Three general types of commercial products within the scope of the invention can be recognized.

1. The oil produced by incorporating a catalytic gel into a raw oil such as linseed oil with the minimum amount of heat required to produce a clear homogeneous oil. (This oil could be sold as such to varnish makers.)

2. The above oil in which the gel has been thoroughly dispersed and the product further conditioned by further heat treatment. (This oil could be used in undercoaters and enamels as such.)

3. Varnishes produced from either the oil produced by 1 and 2 above by incorporation of varnish resins before and/or after the heating of the oil.

We claim:

1. The process which comprises gelling an oil of the class consisting of oiticica oil, perilla oil, dehydrated castor oil and mixtures of said oils with less than an equal quantity by weight of linseed oil by treating said oil with a gelation catalyst of the class consisting of hydrogen fluoride and boron fluoride at a moderate temperature and in sufficient quantity to form a gel of about the consistency of art gum, and dispersing the gel so formed, with the aid of a dispersing agent, in an oil of the class consisting of unbodied drying and semi-drying oils by distributing the gel throughout the oil in which it is to be dispersed, the particles of the gel as dispersed being no larger than small lumps, and heating the mixture to a temperature of at least around 500° F.

2. The process which comprises gelling an oil of the class consisting of oiticica oil, perilla oil, dehydrated castor oil and mixtures of said oils with less than an equal quantity by weight of linseed oil by treating said oil with a gelation catalyst of the class consisting of hydrogen fluoride and boron fluoride at a moderate temperature and in sufficient quantity to form a gel of about the consistency of art gum, and dispersing the gel so formed in an oil of the class consisting of unbodied drying and semi-drying oils by milling the gel and thereafter distributing the milled gel throughout the oil in which it is to

be dispersed, and heating the mixture to a temperature of at least around 500° F.

3. The process which comprises gelling an oil of the class consisting of oiticica oil, perilla oil, dehydrated castor oil and mixtures of said oils with less than an equal quantity by weight of linseed oil by treating said oil with a gelation catalyst of the class consisting of hydrogen fluoride and boron fluoride at a moderate temperature and in a quantity of from about .01 to 1.0%, and dispersing the gel so formed in an oil of the class consisting of unbodied drying and semi-drying oils by distributing the gel throughout the oil in which it is to be dispersed, the particles of the gel as dispersed being no larger than small lumps, and heating the mixture to a temperature of at least around 500° F.

4. The process which comprises gelling an oil of the class consisting of oiticica oil, perilla oil, dehydrated castor oil and mixtures of said oils with less than an equal quantity by weight of linseed oil by treating said oil with hydrogen fluoride at a moderate temperature and in sufficient quantity to form a gel of about the consistency of art gum, and dispersing the gel so formed in an oil of the class consisting of unbodied drying and semi-drying oils by distributing the gel throughout the oil in which it is to be dispersed, the particles of the gel as dispersed being no larger than small lumps, and heating the mixture to a temperature of at least around 500° F.

5. The process which comprises gelling an oil of the class consisting of oiticica oil, perilla oil, dehydrated castor oil and mixtures of said oils with less than an equal quantity by weight of linseed oil by treating said oil with a gelation catalyst of the class consisting of hydrogen fluoride and boron fluoride at a moderate temperature and in sufficient quantity to form a gel of about the consistency of art gum, and dispersing the gel so formed in unbodied linseed oil by distributing the gel throughout the linseed oil, the particles of the gel as dispersed being no larger than small lumps, and heating the mixture to a temperature of at least around 500° F.

6. The process which comprises gelling otitica oil by treating said oil with a gelation catalyst of the class consisting of hydrogen fluoride and boron fluoride at a moderate temperature and in sufficient quantity to form a gel of about the consistency of art gum, and dispersing the gel so formed in an oil of the class consisting of unbodied drying and semi-drying oils by distributing the gel throughout the oil in which it is to be dispersed, the particles of the gel as dispersed being no larger than small lumps, and heating the mixture to a temperature of at least around 500° F.

7. The process which comprises gelling perilla oil by treating said oil with a gelation catalyst of the class consisting of hydrogen fluoride and boron fluoride at a moderate temperature and in sufficient quantity to form a gel of about the consistency of art gum, and dispersing the gel so formed in an oil of the class consisting of unbodied drying and semi-drying oils by distributing the gel throughout the oil in which it is to be dispersed, the particles of the gel as dispersed being no larger than small lumps, and heating the mixture to a temperature of at least around 500° F.

8. The process which comprises gelling dehydrated castor oil by treating said oil with a gelation catalyst of the class consisting of hydrogen fluoride and boron fluoride at a moderate temperature and in sufficient quantity to form a

gel of about the consistency of art gum, and dispersing the gel so formed in an oil of the class consisting of unbodied drying and semi-drying oils by distributing the gel throughout the oil in which it is to be dispersed, the particles of the gel as dispersed being no larger than small lumps, and heating the mixture to a temperature of at least around 500° F.

9. A product prepared in accordance with the process of claim 1.

10. A product prepared in accordance with the process of claim 6.

11. A product prepared in accordance with the process of claim 7.

12. A product prepared in accordance with the process of claim 8.

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Certificate of Correction

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HENRY G. BERGER ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 1, line 32, for the word "reading" read *readily*; column 6, line 60, for "1/4 hour" read *1 1/4 hours*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of July, A. D. 1947.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.