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THIXOTROPIC OIL VEHICLE

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The present invention relates to a process for producing oil vehicles possessing thixotropic characteristics thereby inducing in the vehicle improved brushing characteristics and imparting thereto nonsagging characteristics when the vehicle is used in coating materials such as paints and varnishes.

In an application for patent filed December 11, 1957, under Serial No. 701,961 by Schroeder, Terrill and Hauge, there is described an oil vehicle which possesses improved and desirable properties since thixotropic characteristics have been added to the oil vehicle by reaction with a specific chemical compound, namely, ethylenediamine. In that application it has been shown that oil vehicles generally, that is to say, drying oils, semidrying oils, as well as the homopolymers and copolymers thereof, are improved as to certain desirable characteristics normally associated with the phenomenon of thixotropy, by reaction with ethylenediamine.

The present invention deals with an improved procedure for imparting to such specified oil vehicles the desired and improved thixotropic characteristics.

In accordance with the present invention, the oil vehicle, whether the same be a drying oil, a semidrying oil, a homopolymer or copolymer thereof, is first reacted with a considerable amount of ethylene diamine to prepare what may be designated as an ethylenediamine-oil concentrate which latter may thereafter be blended and reacted with the specified oil vehicle in order to impart thereto the thixotropic characteristics.

By first preparing an ethylene diamine-oil concentrate containing from 0.7 to 15%, and preferably about 5% ethylene diamine under controlled heating, there is produced in accordance with the present invention a material of thixotropic or paste-like consistency. This material can be subsequently incorporated into an oil or vehicle to achieve an oil or vehicle of prescribed thixotropy at a lower level of ethylene diamine than was required heretofore and, furthermore, with the production of an end product of better color, greater tolerance for mineral spirit diluents and of less odor.

Whereas in said Serial No. 701,961, filed December 11, 1957, it is indicated that a specified thixotropic characteristic may be imparted to the oil when employing from 1 to 5% of ethylenediamine, in accordance with the present invention, the ultimate ethylenediamine concentration will vary within the limits from about 0.1% to about 1.5%. In order to prepare the desired end product, one first prepares a concentrate in which the ethylenediamine is combined with the same oil vehicle as is desired in the ultimate composition or one may prepare an ethylenediamine concentrate of another oil vehicle and employ that concentrate as the additive for the vehicle, the thixotropic characteristics of which it is ultimately desired to control. When one employs the latter procedure, it is recommended, by reason of cost, ease of operation and lack of an undue amount of initial and final discoloration, to react the ethylenediamine with a bodied ester of linseed oil, as for instance the tripentaerythritol ester. The latter may be prepared either by reaction of the tripentaerythritol with the higher unsaturated fatty acids, which may be those found in lin-

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seed oil, rather than by the reaction of the triglyceride of such fatty acids with the tripentaerythritol, in an attempt completely to transform the triglyceride ester to an ester of tripentaerythritol.

The following examples are given merely as illustrative of the invention and are not deemed to be limitative thereof.

EXAMPLE 1

A suitable higher fatty acid ester from which can be prepared the ethylenediamine concentrate of the present invention was prepared by reacting 800 parts by weight of the free fatty acids of linseed oil with 128 parts by weight of tripentaerythritol by heating the same together in contact and under agitation at an esterifying temperature of 450 to 500° F. until the acid value of the mixture indicated that esterification was substantially complete, all in conventional manner.

The resultant ester was then preferably bodied by heating the same at bodying temperature of about 575° F. until the desired viscosity was achieved. In this instance, the heating was continued until a viscosity of approximately 36 poises was obtained.

There was added to 190 parts by weight of the bodied ester prepared as indicated above, contained in a 3-necked flask equipped with thermometer, stirrer, reflux and separatory funnel, 10 parts by weight of ethylenediamine in small increments over a period of about ½ hour at a temperature of about 240° F. Thereafter the temperature was maintained elevated but below 250° F. for an additional hour and then increased to 320° F. and held for three hours in order to obtain final reaction between the ethylenediamine and the ester. If the temperatures be greatly in excess of those specified, the end product will tend to possess an undesirable dark color than if prepared as indicated above.

This concentrate may then be employed as a control agent and additive for an oil vehicle, the thixotropic characteristics of which it is desired to change, as for instance a vegetable oil, specific examples of which may be bodied or unbodied drying oils, and semidrying oils, and even for nondrying oils, or as an additive for copolymers of such vegetable oils. The thixotropic characteristics desired can be obtained by reaction at 100% nonvolatile content, i.e., without solvent, or the reactant materials may be dissolved in the usual paint and varnish solvents, as for instance so-called mineral spirits.

EXAMPLE 2

As an example of the preparation of a drying oil vehicle having thixotropic properties, 200 parts by weight of tung oil was heated with 39 parts by weight of the bodied tripentaerythritol-linseed oil fatty acids ester (1% by weight ethylenediamine) made in Example 1, at a temperature of 320° F. and held for blending and reaction at that temperature for ½ hour.

The thixotropic characteristics of the product so prepared are listed below at 100% nonvolatile content, at 50% nonvolatile content, and 30% nonvolatile content, the solvent being mineral spirits.

Table 1.—Brookfield readings

100% NONVOLATILE		
R.p.m.	Increase	Decrease
6	1,000	1,000
12	500	500
30	200	200
60	100	100

The thixotropy may be expressed as 1000/100.

50% NONVOLATILE

R.p.m.	Increase	Decrease
6	960	600
12	450	310
30	120	140
60	75	80

The thixotropy may be expressed as 960/80.

30% NONVOLATILE

R.p.m.	Increase	Decrease
6	300	45
12	130	30
30	30	20
60	19	14

The thixotropy may be expressed as 300/14.

Color at 100% nonvolatile—14+ Gardner color.

EXAMPLE 3

In Example 2 an oil vehicle comprised essentially of tung oil and having approximately 1% by weight total ethylenediamine was prepared. In this example, tung oil reacted directly with 1% by weight ethylenediamine was prepared in accordance with the procedures outlined in said Serial No. 701,961.

To 400 parts by weight of tung oil was added 4 parts by weight of ethylenediamine in small increments over a period of ½ hour and at a reaction temperature of 240° F. and subsequently heated to 320° F. and held at temperature for approximately 4 hours or until the ethylenediamine had reacted. The end product at 100% nonvolatile content exhibited the following thixotropic characteristics as determined in the usual way on a Brookfield instrument at the specified increasing rate of agitation and with decreasing rate of agitation, all as shown in Table 2.

Table 2

100% NONVOLATILE

R.p.m.	Increase	Decrease
6	60	20
12	25	15
30	7	8
60	6	6

The color of this product was dark brown, hazy, and possessed a color which was extremely undesirable as compared with the color of the product of Example 2.

EXAMPLE 4

It will be understood that the fatty acids of other drying oils or the higher unsaturated fatty acids generally, may be esterified with a polyhydric alcohol having 3 or more hydroxyls and such ester then combined with ethylenediamine as indicated above, to produce a desirable concentrate.

A distilled fraction from tall oil, which consists essentially of the higher unsaturated fatty acids, represents an excellent vehicle from which one may prepare the desired ester, as for instance an ester prepared from glycerine and other polyols having 3 or more hydroxyl groups in the molecule. Thus 100 parts by weight of such tall oil fraction is heated with 13.4 parts by weight of pentaerythritol to esterify the same and the resulting ester then heated as indicated above with 5% by weight of ethylenediamine to prepare a concentrate. This concentrate can be employed to impart thixotropic characteristics to the oil vehicles mentioned above.

EXAMPLE 5

An ethylenediamine concentrate was also prepared by preparing the tri-ester of the fatty acids of cottonseed oil with tripentaerythritol. This was done by heating the fatty acids in the conventional way with sufficient tripentaerythritol completely to esterify the same, namely, 3000 parts by weight of the free fatty acid and 538 parts by weight of tripentaerythritol. The resulting ester was bodied by heating at bodying temperature, namely, about 590° F. until the viscosity had increased to about Z2+½ as determined at the bodying temperature, or about Z4+¼ at room temperature. This corresponds to approximately 65 poises.

To 324 parts by weight of the so bodied ester there was added slowly and over a period of about ½ hour, 17.5 grams of ethylenediamine, the temperature of reaction being about 240° F., the mixture then being heated to 320° F. and held there for final processing.

This concentrate could be employed in the same manner as the concentrate of Example 1, for controlling the thixotropic characteristics of oil vehicles.

EXAMPLE 6

There is illustrated below the specific action of the concentrate of Example 5 upon a copolymer of vinyl toluene and polymerized soybean oil. The copolymer was prepared in an environment to produce a final copolymer at approximately a 60% nonvolatile content and to this end, 1300 grams of soybean oil polymerized to a viscosity of Z2 was mixed with 1333 grams of odorless mineral spirits and heated to 320° F. There was then added, in small increments, over a 2 hour period, a mixture of 620 grams vinyl toluene, 80 grams divinyl benzene and 14 grams ditertiary butyl peroxide as polymerization catalyst, and the mixture maintained at 320° F. for an additional 4 hours.

This procedure represents a conventional copolymerization operation with the production of a vinyl toluene-soybean oil copolymer and may be applied to copolymers in the concentrated range 40 to 80% triglyceride oil and 60 to 20% reactive vinyl compound such as the aromatic vinyl compounds styrene, dimethyl benzene and vinyl toluene.

The nonvolatile content as determined was 61.55%. The miscibility limit with odorless mineral spirit was 8.4 parts odorless mineral spirits to one part of copolymer. The viscosity of the 61.55 nonvolatile product was determined as Y+¼. The color on the Gardner scale was 7.

600 parts by weight (61.55% nonvolatile) of the above copolymer was reacted by heating at 230° F. and reacting it in contact and under agitation with 30 parts by weight of the cottonseed oil ester-ethylenediamine concentrate above described in Example 5. This heating was continued until processing was completed, the temperature raised to 320° F. and held for an additional ½ hour. The final sample was reduced with odorless mineral spirits to a nonvolatile content of 47.7%.

The solubility limit of the resulting product was 7.6 parts odorless mineral spirit to one part copolymer solids. The color was 7+-. The final concentration of ethylenediamine was 0.6% based on vehicle solids.

The thixotropy as determined by Brookfield viscosimeter is shown in Table 3:

Table 3

R.p.m.	Increase	Decrease
6	400	120
12	250	80
30	120	54
60	81	40

The thixotropy may be expressed as 400/40.

A sample of the soy oil-vinyl toluene copolymer treated directly with ethylenediamine to the extent of 0.6% gave

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a product having a thixotropy of 8/5, a color Gardner 9 and an odorless mineral spirits miscibility limit of 4.8 to 1.

Whereas in Serial No. 701,961 mentioned above, ethylenediamine is the aliphatic diamine capable of imparting thixotropic characteristics to an oil vehicle, in the present invention it is possible to employ in the manufacture of the concentrate, hexamethylene diamine. As an example, the fatty acids of linseed oil may be esterified with tri-pentaerythritol and bodied in the usual manner as indicated above. A concentrate may be prepared by reacting 324 parts by weight of such bodied ester with 29 parts by weight of hexamethylene diamine in the same fashion as indicated above, and such concentrate employed in identical fashion as the concentrate made with ethylene diamine.

In accordance with the present invention, thixotropic characteristics can be imparted to various oil vehicles by the incorporation therein of sufficient concentrate to produce an amine concentration in the final product of from about 0.1% to 1.5% in contrast to the range in the concentrate of from 0.7% to 15% and preferably in the neighborhood of about 5%.

It is interesting to note that the concentrates of the instant invention possess such inherent capacity for imparting thixotropic properties that a few percent of such a concentrate will produce a jelly-like material when mixed with regular gasoline, mineral spirits, odorless mineral spirits, varnish makers, and painter's naphtha. To produce such a jellied product, the concentrate, as for instance that produced in Examples 1, 4, or 5, is heated until quite liquid, and poured into gasoline or the other solvents mentioned, the mixture stirred vigorously and allowed to cool. 100 grams of gasoline can be set to a jelly when employing 11.7 grams of the 50% nonvolatile linseed oil acids-tripentaerythritol ester-ethylenediamine concentrate.

What is claimed is:

1. The process of preparing an oil vehicle possessing thixotropic characteristics which comprises (a) reacting by heating below about 320° F. an aliphatic diamine selected from the class consisting of ethylene diamine and hexamethylene diamine with an ester of a drying oil fatty acid and a polyol having at least three hydroxyl groups until a reaction product concentrate is obtained, the amount of said diamine being from about 0.75% to 15% based on the weight of the ester and (b) then heat-blending said reaction product concentrate with a drying oil vehicle selected from the class consisting of fat drying oils, fat semidrying oils, heat-bodied fat drying oils, heat-bodied fat semidrying oils and copolymers of any of the former

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with an aromatic vinyl monomer, the amount of reaction product concentrate so heat-blended being sufficient to produce in the final blended oil vehicle a diamine equivalent of 0.1% to 1.5%.

2. Process in accordance with claim 1 wherein the concentrate product is prepared from an ester of linseed oil acids and tripentaerythritol.

3. Process in accordance with claim 1 wherein the concentrate product is prepared from the tri-ester of tung oil acids and glycerine.

4. Process in accordance with claim 1 wherein the concentrate product is prepared from an ester of tall oil acids and pentaerythritol.

5. Process in accordance with claim 1 wherein the concentrate product is prepared from an ester of cottonseed oil acids and tripentaerythritol.

6. Process in accordance with claim 1 wherein the concentrate product is prepared from a bodied ester of a polyol having at least three hydroxyl groups and fat acids of an oil having drying characteristics.

7. Process in accordance with claim 1 wherein the concentrate product is prepared from an unbodied ester of a polyol having at least three hydroxyl groups and fat acids of an oil having drying characteristics.

8. Process in accordance with claim 1 wherein the concentrate product is prepared from hexamethylene diamine.

9. Process in accordance with claim 1 wherein the diamine is ethylene diamine and the amount thereof employed is 3% to 7%.

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