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MODIFICATION OF FATTY OILS

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GENERAL FIELD OF INVENTION

The invention relates to "modification of organic isocolloids," and to the modified products.

By "isocolloids" I mean organic colloidal substances containing mixtures of unsaturated carbon compounds. The dispersed phase and the dispersion medium of these colloidal systems are both of the same chemical composition but in a different physical state. Organic isocolloids are mixtures of chemically similar organic compounds wherein one or more of those compounds, serving as dispersed phase, are dispersed or dissolved in the others which serve as the dispersion medium of this isocolloid system. With such isocolloidal systems (or organic isocolloids) it is possible, by "modification," to change the relative concentration of the dispersed phase and the dispersion medium. For instance, it is possible to increase the dispersed phase concentration, in which event the amount of the dispersion medium will be correspondingly reduced.

The colloidal transformation brought about in accordance with the invention apparently involves an alteration in the number, size or physical state of the colloid aggregations (micelles).

Briefly summarized, the processes according to my invention contemplate dispersion of a modifying agent in the organic isocolloid, and usually also the application of heat. In this way "modification" is brought about and various characteristics and properties of the starting materials are altered, the nature and degree of alteration depending upon the treatment and also upon the nature of the isocolloid used as starting material.

Some of the more important effects of the colloidal transformations incident to modification are, for example, in the case of fatty oils, changes in drying characteristics, body, viscosity, melting point, elasticity, film strength, etc.

Other changes may also be brought about by treatment in accordance with my processes.

There are many types of organic isocolloids capable of treatment in accordance with the broad aspect of the invention, for instance, fatty oils, fatty acids and materials containing the same, i. e., glycerides of fatty acids whether or not such glycerides also contain other acids; also resins, waxes, tars, pitches, etc.

The present invention is particularly concerned with modification of glycerides of fatty acids, such as fatty oils, examples of which are given hereinafter.

In accordance with the broad aspect of the invention, many different materials and classes thereof may be employed as modifying agents. In general, these materials are electrolytes or polar compounds. The present application is directed to the use of organic acids as modifying agents for glycerides of fatty acids, such as fatty oils.

Various features of my improved processes are disclosed and claimed in copending applications, some of which are mentioned hereinafter. The subject matter claimed in the present application is also disclosed in my prior applications Serial No. 397,279, filed June 9, 1941, and Serial No. 318,650, filed February 12, 1940. These two applications are continuations of earlier applications including Serial Nos. 188,014 (Patent 2,244,666), 359,425 (Patent 2,213,944), and 143,786 (Patent 2,189,772).

The Starting Material

The fatty oils and similar materials with which the present application is especially concerned find one of their most important uses in the varnish industry, where oils having good body and drying power are very important. The improved products produced in accordance with this invention also have many other uses.

A list of typical oils which may be advantageously modified by my invention is as follows:

Tung oil	Rapeseed oil
Castor oil	Walnut oil
Linseed oil	Pine seed oil
Fish oil (train oils)	Corn oil
Poppyseed oil	Olive oil
Sunflower oil	

The ease of transformation or modification, under equal conditions, decreases in the order given. That is, the first mentioned oils are most rapidly modified by my methods, while the oils at the end of the series are modified more slowly. However, it should be also mentioned that by the employment of suitable modifying agents in my methods, even the last mentioned oils (those at the end of this series) can be profoundly modified, as well as those oils appearing in the first of the series.

The foregoing listed, and other fatty oils may be classified as follows:

Drying oils	Semi-drying oils
Tung oil. Oiticica oil. Linseed oil. Perilla oil.	Sunflower oil. Poppyseed oil. Soya bean oil. Walnut oil. Rapeseed oil. Pine seed oil.

Non-drying oils	Special oils
Olive oil. Corn oil. Cottonseed oil. Coconut oil.	Hydroxylated; castor oil, etc. Fish oils (train oils).

The fish oils are mixtures of non-drying and drying triglycerides.

In accordance with the invention, the oils referred to may be treated per se, or they may be treated in mixtures containing more than one

such oil, or containing other materials. For instance, synthetic resins containing natural resins or acids of fatty oils and of resins, may be modified in accordance with the invention.

In addition, separated fractions of fatty oils (for instance, the better drying fractions) may be used as starting materials, either alone or mixed with other oils.

The Modifying Agent

As hereinbefore mentioned, the present application is particularly concerned with the use of organic acids as modifying agents or polar compounds. Such acids may be grouped in various ways, it being mentioned that both aliphatic and aromatic organic acids are useful in my processes, especially those which are lower molecular acids.

In accordance with the foregoing classification, examples are as follows:

Aromatic	Aliphatic
Salicylic	Formic
Sulpho salicylic	Acetic.
Phthalic	Oxalic
Benzoic	Monochloracetic
2:3 hydroxy naphthoic	Trichloracetic
	Malonic
	Lactic
	Propionic
	Butyric
	Crotonic
	Malic
	Maleic
	Succinic
	Tartaric
	Isovaleric
	Citric
	Capric
	Hydroxyacetic

For most purposes, I prefer to employ relatively low molecular acids, having not more than eleven carbon atoms.

Carboxylic acids are of especial utility, particularly polycarboxylic. One of the best groups is dicarboxylic acids. The carboxylic acids may be grouped as follows:

Monocarboxylic	Polycarboxylic	
	Dicarboxylic	Tricarboxylic
Butyric	Oxalic	Citric
Propionic	Tartaric	
Isovaleric	Maleic	
Capric	Phthalic	
Crotonic	Malonic	
Lactic	Succinic	
Salicylic	Malic	
Sulpho salicylic		
Acetic		
Formic		
Benzoic		
Naphthenic		
Trichloracetic		
Monochloracetic		
Hydroxyacetic		
2:3 hydroxy naphthoic		

Although the acids themselves may be used, where the anhydride is commercially available, I prefer to use that form of the polycarboxylic acids. For example, phthalic, maleic and succinic anhydrides are available.

The polycarboxylic acids, especially dicarboxylic acids having not more than eight carbon atoms, are particularly suitable for improving the drying qualities of oils, especially fatty oils of the three classes commonly referred to as non-drying, semi-drying and drying. Examples of these three classes of oils are—castor oil, soya bean oil and linseed oil, respectively.

Organic acids are especially advantageous in modifying fatty oils. For one thing, the modified fatty oil products obtained with the aid of such acids, dry faster. That is, they have an increased drying velocity as compared with the original oil. This is advantageous in modifying non-drying and semi-drying fatty oils, as well as in treating drying oils. Further, in addition to increasing the drying velocity, organic acids also increase the rate of bodying of fatty oils in most cases. That is, fatty oils bodied in the presence of organic acids have a greater body than that of the same oil bodied, alone, under the same conditions.

Treatment Conditions

The first step of the process is to mix the modifying agent with the organic isocolloid to be modified, and to produce an intimate admixture of the two materials. Solid organic acid modifying agents may be added in the form of a dry powder. In such cases, it is advantageous to mill the dry modifying agent with the starting material (organic isocolloid) using any of the known mills, etc., for producing a colloidal dispersion. If the organic isocolloid is a liquid, such as an oil, the mills used for grinding inks, paints and the like, may be employed. In this way, the solid polar compound may be ground into and dispersed in the oils, etc. to be modified. Other methods of dispersing or dissolving the polar compounds in the organic isocolloids may also be used. For instance, both the polar compound and the organic isocolloid may be dissolved in a suitable solvent. Again, liquid polar compounds may be directly mixed with the oils by stirring.

The organic isocolloid and the polar compound may be mixed cold; that is, at room temperature, when the polar compound is directly soluble in the organic isocolloid. In such cases, at least some modification may be obtained.

Again, the polar compound and the organic isocolloid may be simply melted together or fused into a homogeneous mass, if both are readily fusible and miscible with each other. Here too, a modified product is directly obtained.

When employing organic acids, the mixture of the isocolloid starting material and the polar compound is preferably heated, the treatment temperature being maintained for a shorter or longer period of time, depending upon the nature of modification desired.

Although many modifying agents are capable of use throughout a wide percentage range (for instance from a fractional percentage up to about 30%), the organic acids should ordinarily be used in amounts not over about 10%, for instance, from about .01% to about 5% (based on the starting material), the preferred range being from .01% to .9%.

As to the temperatures employed, they may be varied over a wide range, although the best results are obtained at temperatures considerably above room temperature but below the boiling point of the isocolloid. When using organic acids the temperature should be above about 200° C., and preferably from about 250° C. to 310° or 320° C.

The time of treatment may also be varied, depending upon the starting material, the treating agent and the result desired. In general, increasing the time of treatment results in more extensive modification. The treatment temperature should ordinarily be maintained for at least thirty minutes, and preferably for several hours.

The heating of the oil in the presence of the polar compound or electrolyte (modifying agent) may be done in open vessels and at atmospheric

pressure. However, advantageous results are obtained when the heating is carried out in closed vessels, such as kettles, autoclaves, pipe coils, etc., to secure the desired modification with the aid of the polar compound. In such cases, the heating may be carried out under reduced or increased pressure with advantage, depending upon the results desired. For instance, heating the mixture under reduced pressure or vacuum, advantageously influences the modification in some circumstances. Likewise, heating under positive (superatmospheric) pressure also is advantageous (and influences the modification) as when volatile solvents or volatile or unstable polar compounds or both are used and the mixture heated above the normal boiling point of such materials. Heating under pressure is also advantageous with certain oils, such as tung oil and the like. For one thing, the pressure assists in preventing the coagulation or gelling of tung oil which ordinarily occurs when tung oil is heated to 260°–280° C.

SUPPLEMENTAL TREATMENT CONDITIONS AND AGENTS

My processes may be practiced in the absence of any additional material, other than the electrolyte or polar compound. However, I have found it is advantageous in some cases to incorporate the electrolyte in the presence of additional materials which facilitate its incorporation and the modification of the organic isocolloid. For instance, the electrolyte may be incorporated in the presence of various organic bodies such as the purely organic additions mentioned post or organic solvents. Again metal soaps may also be added; for instance siccatives (driers) such as the resinates and linoleates of metal compounds and metal oxides, commonly used in the varnish industry, as is mentioned in Serial No. 143,786. Further, sulphur or sulphur compounds, such as sulphur chloride, etc., may also be used in these processes and added in addition to the polar compound during the reaction or as an after treatment. The sulphur or sulphur compounds effect further modification and produce sulphurized products. The temperature usually employed for modification (above 200° C.) being substantially above normal vulcanization temperatures, the effect of the sulphur treatment at modifying temperatures is quite different from vulcanization.

However, I may also effect vulcanization of my modified products in an after treatment, so as to produce solid, coherent and elastic products, similar in some characteristics to ordinary rubber. Sulphur may be used for this purpose and may be added as such, or in the form of a sulphur compound, such as sulphur chloride, etc. The action of the sulphur is analogous to that which takes place in the vulcanization of rubber. Thus, accelerators or activators (zinc oxide, etc.) or both, such as usually employed in the vulcanization of rubber, may be used in my processes to accelerate vulcanization when sulphur, etc. is added. The added sulphur vulcanizes or sulphurizes my modified products further changing their properties.

When making solid vulcanized rubber-like products, I employ temperatures between 120° and 180° C. for vulcanization, and from 5 to 50 parts of sulphur to 100 parts of the isocolloid under treatment. This vulcanization should be effected after modification, and accelerators and antioxidants may be added to the mix in known manner. I may produce liquid vulcanized products as well as rubber-like solids, by regulating the amount of sulphur and the time and temperature of heating. The liquid products are useful as varnish or paint bases.

Two step methods for making vulcanized, modified, heat-bodied fatty oil products are described and claimed in my application Serial No. 236,800 (Patent 2,234,545). As there stated, many of those products are useful as "rubber substitutes." Others are useful for other purposes, for instance, in the manufacture of varnishes, lacquers and other liquid coating compositions, as well as in plastic compositions.

As noted above, the processes may be carried out in various ways, for instance, either in open or closed vessels as desired. In the latter case, the air can be entirely or partially displaced by another gas, such as hydrogen, CO_2, SO_2, H_2S, nitrogen, etc., which influence the results obtained, these gases being used in supplement to the primary modifying agent employed. Again, in both cases such gases may be passed through the material being treated. That is, the modification can be carried out during the passage of a gas. The gas pressure can be that of atmospheric. In many cases, however, a vacuum may be used with advantage. Again, even a higher pressure of several atmospheres is to be recommended in certain cases, it being sometimes advantageous.

That is, I have further found that the results of the process vary with the nature of the gas present and also with the physical condition (pressure) of this gas. Thus I have found that a certain given starting material which is initially liquid will become slightly viscous only as a result of the electrolyte treatment, if the latter is effected under atmospheric pressure (open vessel) but more viscous if the gas is rarefied by the employment of a partial vacuum. In other cases the converse applies. When plus pressure was used the results differ again. Air gives a different result from another gas or mixtures of gases such as mentioned ante. The electrolyte treatment may be carried out either in the total or partial absence of air, by replacing the same with another gas, such as those shown ante.

A pressure treatment followed by a vacuum treatment may be used, and I have found it to be advantageous to use alternately, atmospheric or plus pressure and vacuum treatment. Such alternate treatment increases the uniformity of the distribution of the electrolyte in the organic isocolloid. In my processes, the gas may be blown or passed through the liquid mass or simply passed over the surface of the same during the heating. It is advisable in some cases, both when open or closed vessels are employed to have a constant passage of the gas, such as those given ante, during the treatment with electrolyte.

It may be stated with reference to the action of gases, that generally speaking rarefication of the gases present, by reduction of pressure in the vessel in which the treatment is given, tends to intensify the action of the gases in my processes.

If desired, the electrolyte may be produced in situ, that is, within the organic isocolloid under treatment, by interaction within the organic isocolloid, of substances capable of reacting under the conditions of the process to produce the electrolyte. The same applies to the gas in the presence of which the organic isocolloid is to be treated and a substance or substances may be added which evolve the desired gas during the processing. It has been found in certain cases that electrolytes and gases which are produced in situ,

being in the nascent state, are somewhat more active than those added in the pre-formed state.

Likewise, the organic isocolloid itself may be formed in situ during the treatment. That is, if it is desired to modify an organic isocolloid which is not a naturally occurring material and which has to be produced before it can be treated, the production of such artificial or manufactured organic isocolloid may be advantageously combined with the treatment with the electrolyte. For instance, in making modified heat-bodied fatty oils, the oil may be both heat-bodied and modified in a single step by heat-bodying the fatty oil in the presence of the electrolyte or polar compound. To do this several hours heating at polymerization temperatures is required. Many of my electrolytes are advantageous for this purpose as they accelerate the heat-bodying and polymerization of fatty oils.

In addition to the action of electrolytes and the cooperating action of gases in effecting the colloidal transformations characteristic of my invention, an additional modification of the ultimate physical properties of the treated products can be effected by the addition to the material under treatment, of purely (i. e. metal-free) organic bodies, such as phenols, naphthols, naphthalene, chloroform, acetone, alcohols and their homologues and derivatives. These additions are supplemental to the use of electrolytes. Some of them are solvents and assist in dispersing the electrolyte in the organic isocolloid. The use of solvents for this purpose is also shown in my Serial No. 273,159 (Patent 1,985,230) and other prior applications.

I have also found that in my processes the colloidal transformations may be promoted by the use of rays of oscillating energy, such as ultra-violet rays, infra-red rays, X-rays, etc. That is, it is advantageous to irradiate the oil or other organic isocolloid, before or during the treatment with electrolyte. Sometimes a subsequent treatment with these rays is also helpful. Further, these rays influence and intensify the action of the gases in my processes.

EXAMPLES

Example 1

To 100 parts of linseed oil are added 5 parts of salicylic acid and the mixture heated in a vacuum for two hours at a temperature between 300° and 350° C., the vacuum broken and the modified oil poured out and allowed to cool. The modified oil so obtained is useful in making varnishes and other coating compositions.

In Example 1, other oils, such as rapeseed oil, castor oil, etc., may be used in lieu of linseed oil to obtain other modified oil products useful in making varnishes and the like. However, in modifying castor oil with this acid, I prefer to employ a lower temperature, say 270° C., and heat for a longer time. Likewise, in lieu of the salicylic acid, I may employ other organic acids, such as oxalic, tartaric, citric, etc., disclosed ante, in the practice of Example 1.

Example 2

In this example, a castor oil having an acid number of 9, is used as the starting material.

1000 parts of this castor oil are heated with 30 parts of salicylic acid at 270° C., for 5 hours in an open kettle.

The modified oil product so obtained is a heavily bodied oil having an acid number of 11. It can be further treated to reduce its acid number and to increase its body, if desired. In doing so, the oil is further heated at 200° C., while bubbling nitrogen through the oil, for two hours. The oil product so obtained has an acid number of 7 and is a useful paint and varnish base.

Example 3

SERIES OF COMPARATIVE TESTS

To secure comparative results with a number of different organic acids, a series of experiments was conducted each under equivalent conditions. These experiments included not only bodying of the oil in the presence of the organic acid, but also preparation of a varnish with the bodied oil. The bodying of the oil and the preparation of the varnish are described hereinafter under separate headings.

Bodying of Oil

In all experiments, alkali refined linseed oil was used, each batch consisting of 1½ gallons of oil placed in an aluminum 3 gallon (laboratory size) varnish kettle, along with the particular acid modifying agent.

In each case the treatment was terminated as near as practicable at that time when the viscosity had reached a certain pre-selected value (V on the Gardner-Holt varnish scale), thereby giving a comparison of time required to body with the different treating agents.

The manner of heating and treating each batch was as follows:

(*a*) The temperature was raised to about 200° C. in about 30 minutes.

(*b*) The temperature was held for one hour at 200° C.

(*c*) The temperature was raised to 300° C.

(*d*) The temperature was retained at 300° C. for the period of time indicated in Table No. 1 below.

(*e*) CO_2 gas was bubbled through the batch during steps *a*, *c* and *d*.

The holding at 200° C. (Step *b*) was employed to ensure giving opportunity for reaction between the oil and the acid at a temperature below their boiling or sublimation points.

In the case of each acid used, two experiments were conducted, one with ½% of the acid and the other with 5%, as is indicated in the following table:

Table No. 1

	½% acid	Time		Vis.	5% acid	Time		Vis.
		Hr.	*Min.*			*Hr.*	*Min.*	
1	Benzoic acid	3	20	X	Benzoic acid	3	20	Z-1
2	Citric acid anhydrous	2	50	X	Citric acid anhydrous	2	45	W
3	Citric .H_2O	3	15	W	Citric .H_2O	2	30	T
4	Maleic anhydride	2	50	U	Maleic anhydride	2	10	W
5	Oxalic acid anhydrous	3	15	V	Oxalic acid anhydrous	3		X
6	Oxalic .$2H_2O$	3	10	V	Oxalic .$2H_2O$	2	40	W
7	Salicylic acid	3	20	Y	Salicylic acid	2	30	Y
8	Tartaric acid anhydrous	2	30	X	Tartaric acid anhydrous	3		W
9	Blank alkali refined linseed oil	3	45	V	Blank alkali refined linseed oil	3	45	V

It will be noted that certain of the acids were tried both in the anhydrous form and also in the form containing water of crystallization. In each such case the anhydrous form manifests somewhat improved results over the other form. In addition, it may be noted with reference to No. 9 in the above table (blank alkali refined linseed oil) that this represents an experiment conducted under the same conditions, and with the same oil, but without employment of any modifying agent.

Analysis of the foregoing shows that in the series employing ½% of the modifying agent, the ease of bodying varies from a maximum with anhydrous tartaric acid, to a minimum with the blank, as follows:

Tartaric acid anhydrous
Citric acid anhydrous
Maleic anhydride
Salicylic acid
Benzoic acid
Citric acid, $.H_2O$
Oxalic acid $.2H_2O$
Oxalic anhydrous
Blank alkali refined linseed oil

Similarly, with the 5% series, the ease of bodying is as follows:

Maleic anhydride
Salicylic acid
Citric acid anhydrous
Oxalic acid $2H_2O$
Citric acid H_2O
Oxalic acid anhydrous
Benzoic acid
Tartaric acid anhydrous
Blank alkali refined linseed oil

The 5% concentration of modifying agent, in most cases, produces faster bodying than does the ½%, the only exceptions being anhydrous citric acid and anhydrous tartaric acid, which apparently body faster with ½%.

In connection with the above grading of the oils in accordance with ease of bodying, it is noted that the deviations in viscosity from the pre-selected value (V) were ignored and that some of the examples would have occupied different positions in the grading lists had their bodying been terminated exactly at the pre-selected viscosity (V).

The foregoing results indicate substantial improvement in bodying as a result of the employment of a modifying agent. In this connection it should be kept in mind that customarily an effort would be made to body varnish oils to a viscosity as high as from Z4 to Z6 (Gardner scale), which is considerably above the approximate V viscosity pre-selected for testing in the above experiments. In the higher viscosities even better results would be demonstrated. The V viscosity was pre-selected for the present purposes, since preparation of varnishes with oil of this viscosity facilitates measurement of differences in the varnish cooking, the cooking experiments being referred to hereinafter.

Further characteristics of the bodied oils are indicated in Table No. 2 just below:

TABLE No. 2

	Acid	Acid number		Saponification val.		Iodine number	
		½%	5%	½%	5%	½%	5%
1	Benzoic acid	3.3	4.4	194	194	129	122
2	Citric acid anhydrous	3.8	6.0	197	199	134	134
3	Citric acid $.H_2O$	4.1	5.4	195.4	198.4	129	138.5
4	Maleic acid anhydride	4.1	10	196	206	138	145
5	Oxalic acid anhydrous	4.4	5.4	193	196	132.5	135.5
6	Oxalic acid $.2H_2O$	3.0	3.6	204.5	194.5	137	130.3
7	Salicylic acid	4.1	4.1	195	197	143	131
8	Tartaric acid anhydrous	3.6	5.0	200	199	135	131
9	Blank alkali refined linseed oil	3.05		191.7		132	

PREPARATION OF VARNISH

The bodied oil of each experiment referred to in the foregoing series was cooked to a varnish, with each of three different resins:

I. Ester gum (glycerine ester of rosin).

II. Rosin modified maleic alkyl resin (Amberol 801).

III. Rosin modified phenol-formaldehyde resin (Paranol 1750).

In each case the varnish was of 25 gallon oil length (in the proportion of 25 gallons of oil to 100 pounds of the resin), each batch being prepared to yield ½ gallon for laboratory tests. Each batch was thinned with mineral spirits to 50% solids and the cooking time was adjusted so as to yield a viscosity of C to H on the Gardner scale (brushing consistency).

Observations on the bodying of the varnishes with the three different resins are as follows:

I. Ester gum series

In most cases the oils treated with 5% of the acid indicated bodying of the varnishes with ester gum faster than where the oils were treated with ½% of the acid. In this series the varnishes bodied in about three-quarters of the time required for equivalent bodying of a varnish containing the blank control alkali refined linseed oil (bodied without modifying agent). The following showed particularly good results, the list being graded from the top:

	Per cent
Maleic anhydride (best)	5
Benzoic acid	5
Salicylic acid	½
Salicylic acid	5
Oxalic acid, containing crystal water	5

II. Rosin modified maleic alkyd resin series

This series showed the greatest improvement in bodying. Most of the varnishes containing acid treated oils bodied in about one-half the time required for the varnish containing the blank control alkali refined linseed oil. Here again, in most instances, the 5% concentration of modifying agent indicated better results than the ½% concentration. The best were as follows, the list being graded as before:

	Per cent
Maleic anhydride (best)	5
Oxalic acid, with crystal water	5
Anhydrous citric acid	½
Salicylic acid	½
Benzoic acid	5
Salicylic acid	5
Anhydrous citric acid	5

III. Rosin modified phenol-formaldehyde resin series

In this series the varnishes containing acid treated oils bodied in about two-thirds the time required for the varnish containing the blank control alkali refined linseed oil. The best examples are graded as follows:

	Per cent
Maleic anhydride (best)	5
Salicylic acid	½
Salicylic acid	5
Maleic anhydride	½
Benzoic acid	5
Benzoic acid	½
Oxalic acid, with crystal water	½
Oxalic acid, with crystal water	5

All of the foregoing varnishes were also tested for other characteristics, and in most cases displayed improvement in other respects, when compared with the varnishes prepared with the blank control alkali refined linseed oil. To secure comparative results, the same driers were used with each varnish. This drier was as follows:

1. Lead 0.3%
2. Cobalt 0.03%
3. Manganese 0.02%

all as naphthenate solutions, the percentage of metal specified indicating metal content based on the content of oil in the varnish.

The prepared varnishes were then tested for:

(*a*) Drying
(*b*) Cold water resistance
(*c*) Boiling water resistance
(*d*) Alkali resistance

For test purposes the varnish film was applied to a steel plate by means of a spreading knife, providing a film thickness of 0.0015".

Observations of the foregoing tests were as follows:

(*a*) DRYING

In most instances the varnishes containing acid treated oils displayed noticeably improved drying characteristics when compared with varnish containing the blank control alkali refined linseed oil. When considering the varnishes made with all three of the resins above mentioned, the oil treated with ½% anhydrous tartaric acid indicated the best general improvement. Almost equivalent results were shown in the case of the varnishes containing 5% maleic anhydride and 5% salicylic acid.

A second series of comparative varnish tests was conducted with increased drier content both in the blank control varnish as well as in the others (0.8% lead, 0.08% cobalt and 0.04% manganese), but this series displayed results very similar to the above and are, therefore, not separately analyzed herein.

(*b*) COLD WATER RESISTANCE
(*c*) BOILING WATER RESISTANCE

These tests were conducted in accordance with A. S. T. M. standard methods, and reasonably good characteristics were displayed by all of the varnishes.

(*d*) ALKALI RESISTANCE

This test was carried out by immersing test plates (carrying films dried for 48 hours) in a 3% aqueous sodium hydroxide solution. As in the drying tests, the varnish containing ½% tartaric acid manifested the best general improvement with all three resins. Particularly good results were also indicated with ½% anhydrous citric acid and ½% oxalic acid, containing crystal water, when used with the ester gum and the maleic resin.

In connection with the bodying of oils in the comparative series discussed above, it may be mentioned that no glycerine was added to compensate for acidity. Ordinarily, where an appreciable quantity of acid is present, for instance 5%, glycerine should be added to the oils in order to neutralize the excess acidity and lower the acid value. In the foregoing examples, alkali resistance would have been improved by this expedient.

The following additional general observations may be made with reference to the foregoing comparative tests:

1. With respect to drying time, the best results are indicated with ½% anhydrous tartaric acid, 5% maleic anhydride, and 5% salicylic acid.

2. In general, increase in concentration of the acid modifying agent slightly improves drying time, although in a few cases drying was better with the lower concentration.

3. With respect to bodying time, best results are secured with tartaric acid, maleic anhydride, citric acid and salicylic acid.

4. The aromatic acids, such as benzoic and salicylic, are more readily soluble in the oils than are the aliphatic acids. This is a distinct advantage. Although some aromatic acids display a tendency toward sublimation, this tendency is at a minimum with the higher molecular acids such as the carboxylic acids, especially of the naphthalene series, and also of anthracene, anthraquinone, phenanthrene or phenanthraquinone and/or their derivatives.

5. The aliphatic acids have less tendency toward sublimation than do the aromatic acids. (Where appreciable sublimation tends to occur, precautions should be taken to avoid loss of reagent, as by effecting the treatment in a manner to return sublimated agent to the reaction mass.)

Examples 4–10

In another series of comparative experiments certain uniform treatment conditions were adopted, as follows:

In each case, the oil employed was linseed oil and 5% of the treating agent was used.

In each case, the heating time was in the neighborhood of 5 hours. In conducting these experiments the approximate reaction temperature was 300° C., although there were minor differences between various of the experiments. The treatment temperature was between about 290° to 310° C.

A control experiment was also conducted under the same heating conditions, but without treating agent, so as to secure comparative results.

The experiments in this group may be divided into pairs, the two experiments of each pair employing the same treating agent. The difference between the treatment of the two members of each pair was as follows:

1. Heating a 300 gram charge in a one liter distilling flask under vacuum—identified herebelow by the letter (*a*) following the example number.

2. Heating a 150 or 300 gram charge in a 500 c. c. open enameled beaker—identified herebelow by the letter (*b*) following the example number.

Example 4(a)

Citric acid containing water of crystallization

The mixture frothed and bumped slightly during rise in temperature, but then boiled steadily and gradually darkened in color, finally yielding a yellow-brown oil which, on cooling, was a thickish liquid of consistency similar to that of thin treacle.

Example 4(b)

Citric acid containing water of crystallization

Some frothing and gas evolution, and slight bumping occurred, during rise in temperature, but the liquid steadied itself at the treatment temperature (approximately 300° C.). The cooled product was a thick elastic jelly, brown in color with a strong green fluorescence. In the residue, a little of the reagent remained as a charred mass.

Example 5(a)

Oxalic acid

Gas evolution become very rapid during rise in temperature, especially at about 180° C., but the batch steadied with gradual solution of the treating agent. The product was a thinnish oil with a light brown color. A small portion (about 0.75 gram) of the agent remained like sand in the flask.

Example 5(b)

Oxalic acid

The product was similar in color to Example 5(*a*), but slightly thinner.

Example 6(a)

Phthalic anhydride

Some sublimation occurred during rise in temperature and the heating was suspended and then restarted, after which the liquid boiled steadily. The product was a pale yellow material similar in appearance and consistency to vaseline.

Example 6(b)

Phthalic anhydride

Sublimation and suspension and re-starting of heating were as in Example 6(*a*). Boiling continued throughout the reaction and the liquid thickened gradually. The product was a thick viscous oil.

Example 7(a)

Salicylic acid

Some frothing and slight volatilization occurred during rise in temperature. Slight distillation also took place upon reaching treatment temperature, after which the liquid remained steady. The product was a brown oil of the consistency and appearance of syrup.

Example 7(b)

Salicylic acid

Some sublimation occurred at about 230° C., but on reaching reaction temperature slight boiling and gradual thickening took place. The product was a thick viscous liquid of dark brown color.

Example 8(a)

Benzoic acid

During rise in temperature sublimation occurred and vigorous bumping continued for several hours at treatment temperature. After some irregular boiling the liquid steadied. The product was a medium thin brown oil, with a green fluorescence.

Example 8(b)

Benzoic acid

Sublimation occurred during rise in temperature and on reaching treatment temperature the oil boiled gently and gradually thickened. The product was a thick viscous product similar to that of Example 7(*a*).

Example 9(a)

Monochloracetic acid

During rise in temperature gas was evolved and some distillation occurred. Upon reaching treatment temperature the mixture boiled steadily, without distillation, and the color darkened. Shortly after reaching treatment temperature distillation again set in and continued for about one hour, but gradually tapered off. The product was a thick brown oil with a strong green fluorescence. The distillate was a black oil with an obnoxious smell.

Example 9(b)

Monochloracetic acid

The product was a mobile brown colored oil, with a strong dull green fluorescence.

Example 10(a)

Amino salicylic acid

At low temperature, in the neighborhood of 70° C., very bad frothing and some distillation occurred, but the batch gradually subsided as treatment temperature was approached and the mixture then boiled vigorously. The product was a fairly thick golden brown oil with a strong green fluorescence.

Example 10(b)

Amino salicylic acid

Considerable frothing occurred as the temperature rose, although the frothing gradually subsided and was steady at the reaction temperature. The product was a thick dark brown oil with a strong dark green fluorescence.

With reference to Examples 4 to 10 inclusive, it is mentioned that the viscosity of all of the products was higher than the product of the blank control experiment. The consistency in most of the cases was recorded and comparison thereof indicates the following graduation in viscosity, the product of highest viscosity appearing at the top of the list:

	Example	
Soft solid	8 (*b*)	Benzoic acid.
	4 (*b*)	Citric acid with water of crystallization.
Thick viscous	10 (*b*)	Amino salicylic acid.
	7 (*b*)	Salicylic acid.
	10 (*a*)	Amino salicylic acid.
	9 (*a*)	Monochloracetic acid.
	11	Beta-oxynaphthoic acid.
Medium viscous (liquid)	5 (*a*)	Oxalic acid.
	6 (*b*)	Phthalic anhydride.
	7 (*b*)	Salicylic acid.
	9 (*b*)	Monochloracetic acid.
Thin liquid	4 (*a*)	Citric acid with water of crystallization.
	8 (*a*)	Benzoic acid.
	5 (*b*)	Oxalic acid.
		Blank control.

As to color, it is mentioned that the following

were as light as the color of the blank control experiment:

Example	
4 (*a*)	Citric acid with water of crystallization.
8 (*a*)	Benzoic acid.
5 (*b*)	Oxalic acid.

Varnishes were cooked, under equal conditions, from all of the products of Examples 4 to 10. In each case the varnish was prepared in the proportion of 25 gallons to 100 pounds of lime hardened rosin. These varnishes were comparatively tested with a varnish made with the oil produced in the blank control experiment (linseed oil bodied without treating reagent).

In drying tests (without driers), a number of the varnishes showed faster drying than the varnish made with the blank control oil. For instance, the following were faster drying:

Example	
4 (*b*)	Citric acid with water of crystallization.
7 (*b*)	Salicylic acid.
6 (*b*)	Phthalic anhydride.
8 (*b*)	Benzoic acid.
10 (*b*)	Amino salicylic acid.

Example 11

5% of beta-oxynaphthoic acid was added to 300 grams of linseed oil and the mixture heated under vacuum for about 5 hours at from 290° to 300° C. The mixture frothed considerably at the start and upon reaching about 130° C. a fairly violent reaction took place, this reaction subsiding at about 150° C. and giving way to a rapid gas evolution and apparent gradual solution of the reagent. Upon further increase in temperature, to about 270° C., some distillation took place, but this stopped by the time the boiling temperature was reached, and upon attaining the reaction temperature the batch remained steady throughout the five hour treatment period.

The product was a light brown oil with a strong green fluorescence.

Example 12

1000 parts of the same castor oil as used in Example 2 (having an acid number of 9) were heated with 2 parts of sulphosalicylic acid and 20 parts of glycerine, in an autoclave, to 270° C. while slowly bubbling CO_2 through the mixture and maintaining a vacuum of 50 mm. Hg on the autoclave. The mixture was so heated at 270° C. under vacuum for one hour. Then the temperature was reduced to 250° C. and the mixture maintained at that temperature for two hours. Finally the temperature was dropped to 200° C. and the mixture held at this temperature until the modification was completed, about two hours at 200° C. being required. During all of these heatings, the introduction of the CO_2 gas was so controlled as not to destroy the desired vacuum.

The modified castor oil so obtained has good drying properties and an acid number of 3.2. It is useful in making paints and varnishes.

In the above specification the increased drying velocity of oils, e. g. if treated according to the disclosed processes with modifying agents, means always a comparison with an oil, treated in the absence of such polar compounds, but otherwise under similar conditions. The oils, when heated to polymerizing temperatures, change their body, viscosity and to lesser degree also their drying velocity. The action of the polar compounds may be observed if we compare the resulting product to an oil, treated under similar conditions, heated to the same temperature and for the same time, but in the absence of polar compounds. The increased rate of drying frequently causes also an increased rate of bodying of the oils, all other conditions being equal.

During my processes complex changes usually occur, in the presence of acidic polar compounds as a result of which new, improved modified products are obtained from fatty oils, resins and the other isocolloids as described ante as useful starting materials in my processes. For instance, if oils, resins and other compounds containing high molecular acids or derivatives of such acids are heated to temperatures above 200° C. water and hydrogen may be given off by the starting material, accompanied by complicated changes in those starting materials, such as condensation, polymerization, shifting of double bonds, dehydroxylation, decarboxylation, amongst others. In any event in my processes such changes as result in increasing the drying velocity and effecting other improvements in the properties of the starting materials are accelerated by the presence and action of my aforesaid polar compounds; at least beneficial and desirable results are obtained, although it is impossible to ascertain the exact mechanism by which they are obtained in each particular commercial embodiment of my present invention.

I claim:

1. In the manufacture of improved, modified products, suitable for plastic and coating compositions, from fatty oils, fatty acids, esters of fatty acids, and from material containing the same, said modified products having increased drying velocity and other improved properties, the step which comprises heating said materials in the presence of a minor amount of an organic acid at a temperature of at least 200° C. and for a time sufficient to modify the physical properties of and increase the drying velocity of said materials, said heating being continued for at least thirty minutes and the amount of said organic acid being not more than 5%.

2. The process of claim 1, wherein the organic acid is an aromatic acid.

3. The process of claim 1, wherein the organic acid is an aliphatic acid.

4. The process of claim 1, wherein said material is a fatty oil and wherein the organic acid is a carboxylic acid.

5. The process of claim 1, wherein said material is a fatty oil and wherein the organic acid is a polycarboxylic acid.

6. The process of claim 1, wherein said material is a fatty oil and wherein the organic acid is a dicarboxylic acid.

7. The process of claim 1, wherein the organic acid is salicylic acid.

8. The process of claim 1, wherein the organic acid is benzoic acid.

9. The process of claim 1, wherein the organic acid is chosen from the class consisting of maleic acid and its anhydride.

10. The process of claim 1, wherein said material is a fatty oil.

11. The process of claim 1, where said material is a non-drying oil.

12. The process of claim 1, wherein said material is a semi-drying oil.

13. The process of claim 1, wherein said material is a drying oil.

14. The process of claim 1, wherein said material is castor oil.

15. The process of claim 1, wherein said material is soya bean oil.

16. The process of claim 1, wherein said material is linseed oil.

17. The process of claim 1, wherein said material is castor oil and said organic acid is chosen from the class consisting of maleic acid and its anhydride.

18. The process of claim 1, wherein said material is soya bean oil and said organic acid is chosen from the class consisting of maleic acid and its anhydride.

19. The process of claim 1, wherein said material is linseed oil and said organic acid is chosen from the class consisting of maleic acid and its anhydride.

20. The process of claim 1, wherein said organic acid is used in an amount from .01% to .9%.

21. The process of claim 1, wherein said material is a fatty oil and wherein said material is also treated with an alcohol.

22. In the manufacture of improved, modified products, suitable for plastic and coating compositions, from fatty oils, fatty acids, esters of fatty acids, and from materials containing the same, said modified products having increased drying velocity and other improved properties, the step which comprises heating said materials in the presence of a minor amount of an organic acid at a temperature of at least 200° C. and for a time sufficient to modify the physical properties of and increase the drying velocity of said materials, said heating being continued for at least thirty minutes and the amount of said organic acid being not more than 10%.

LÁSZLÓ AUER.

CERTIFICATE OF CORRECTION.

Patent No. 2,298,914. October 13, 1942.

LÁSZLÓ AUER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, second column, line 25, for "alkyl" read --alkyd--; page 7, second column, line 10, for "Example 7(a)" read --Example 7(b)--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of November, A. D. 1942.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)