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PROCESS OF PREPARING EMULSIONS OF
SOAP-FREE FATTY OILS

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In my British Patents 318,562, 321,692, and 341,490 as well as in my United States Patent 2,007,958, I have produced plastic masses out of fatty oils by way of aggregating them in the form of aqueous emulsions. The basic idea of my development program at the time those patent applications were filed, was to convert fatty oils into a rubber-like stage, having properties similar to natural rubber. The products so obtained could be milled and compounded on rubber mills.

According to the present invention, I have prepared by new means aggregated fatty oil emulsions for use in protective coatings, such as varnishes, paints, enamels, etc. The emulsions dealt with in the present application I call "air sensitive emulsions." Under air sensitive emulsions I understand such emulsions, which are sensitive to the action of the air, when exposed to it in form of a thin layer, such as a film, e. g. of 0.0015" to 0.003" wet film thickness; insofar as they contain the fatty oils in the form of solid particles and on the action of the air on their thin layers, as soon as demulsification sets in, they form a solid and coherent film. Such solid film is formed also under such conditions under which a large percentage of the water, originally being the dispersion medium, is still occluded in the film. The film formation is usually reached within a couple of seconds, but latest in a couple of minutes and always in a shorter time than 30 minutes. The non-fluid stage is reached even earlier. In some exceptional cases it may be desirable to slow down artificially the film formation of air sensitive emulsions, so that the film formation should occur within a time exceeding 30 minutes, however, the film formation is rarely slowed to an extent that it should take more than 1 hour. If an air sensitive emulsion is rubbed between the fingers for a minute or so, it will also deposit solid particles or a solid film inbetween the fingers.

Briefly considered, the air sensitive emulsion of the present invention is prepared as an oil-in-water emulsion of which the dispersed phase incorporates a fatty acid ester, such as a fatty oil. The fatty oil is preliminarily bodied to a relatively heavy viscosity and then emulsified, and, in dispersed form, the particles of the fatty oil are treated to effect agglomeration, for instance, by employing hydrogen peroxide, or in other ways as more fully described here below. Advantageously the pH value of the emulsion is retained

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within certain limits during the aggregation treatment. The degree of prebodying and of aggregation of the dispersed particles in situ is such as to render the emulsion highly sensitive to the action of air when spread in thin films and thereby provide for the formation of a coherent solid film immediately upon demulsification of the emulsion.

To explain the importance of my new emulsions, I want to refer to the known facts that if drying oils are used to prepare coating materials, before they form a solid film, they undergo a comparatively slow drying process. Before they form a solid film, they remain for a long period in a liquid stage and reach the so-called "dust-free" stage after a considerable lapse of time. This property of drying oils is causing limitations in their use in protective and decorative coatings and in cases where rapid drying is needed it was necessary to use lacquers, such as nitro-cellulose lacquers. Such lacquers contain more expensive film-forming solids than drying oils and their solvents are also more expensive than those used in connection with drying oils. Now, my new emulsions enable the formulation of very fast drying, almost lacquer-like drying, coating materials, while using as principal film-forming solids drying and semi-drying oils, and utilizing water as principal dispersing agent.

It is old in the art to make emulsion paints, which contain drying oils and drying oil emulsions have been used for many diversified purposes in the past. However, my present invention does not deal with emulsions of drying oils in general, but with quite specific types of emulsions, containing drying oils or semi-drying oils. The dispersed phase of my emulsions has been aggregated and the emulsions possess qualities defined further above as inherent to air sensitive emulsions.

Many investigators consider the process I am calling as aggregation, as polymerization, but I am confident of the fact that actually what occurs in the emulsion is better defined with the expression used by me, that is, by "aggregation." (See article "Polymerization or Aggregation?"—National Paint Bulletin, October, 1937.)

STARTING MATERIALS

The process may be applied to fatty oils generally, including drying oils, semi-drying oils, and

non-drying oils. A typical list of such oils follows:

Tung oil
Oiticica oil
Dehydrated castor oil
Linseed oil
Perilla oil
Sunflower oil
Poppyseed oil
Soya bean oil
Walnut oil
Rapeseed oil
Pineseed oil
Olive oil
Corn oil
Cottonseed oil
Coconut oil
Babassu oil
Hydroxylated oils such as castor oil, etc.
Fish oils (train oils)

It should be noted that, in addition to the natural glycerin esters of the fatty acids, other esters may be employed, such as synthetic glycerin esters of fatty acids, and fatty acid esters formed with other polyhydric alcohols, such as glycols, pentaerythritol, mannitol, sorbitol, etc. In short, natural or synthetic oils may be used, whether of animal or vegetable origin, as well as fractions of either type.

For convenience, all such materials and combinations are referred to herein merely as fatty oils.

As the reaction taking place in my process is a reaction of the polyhydric alcohol esters of unsaturated fatty acids, all such mixed ester type synthetic resins may be used as starting materials for my process, which comprise at least 50% unsaturated fatty acid esters, calculating such portion of the polyhydric alcohol radical into the ester, which is needed to form the esters with the unsaturated fatty acid content of the synthetic resin. Such synthetic resins are, for instance, the alkyd resins of the kind which are mixed esters of polycarboxylic acids and unsaturated fatty acids.

Examples of polycarboxylic acids, forming alkyd resins useful in my process are for instance:

Phthalic acid,
Maleic acid,
Succinic acid,
Malic acid,
Tartaric acid,
Fumaric acid,
Citric acid,
Adipic acid,
Sebacic acid,
Azelaic acid,
Suberic acid, etc., or
Anhydrides of such acids.

Examples of the unsaturated fatty acids, forming alkyd resins useful in my process are for instance:

Linseed oil fatty acids,
China-wood oil fatty acids,
Perilla oil fatty acids,
Oiticica oil fatty acids,
Dehydrated castor oil fatty acids,
Sunflower oil fatty acids,
Soyabean oil fatty acids,
Cottonseed oil fatty acids,
Corn oil fatty acids,
Fatty acids of fish oils (train oils).

The polyhydric alcohols, forming the esters useful as starting materials in this process, should be preferably at least tri-hydric, such as glycerine.

I found that in my process best results are obtained with polyhydric alcohol esters of acids of fatty oils, which esters contain in their acid component at least 50% acids of fatty oils and which fatty oil acids comprise fatty acids having at least two double bonds. In this definition of fatty acid esters, there is included the group of drying and semi-drying fatty oils, further the group of synthetic oils and the group of alkyd resins, not containing more than 50% polybasic acids in their acid component.

Any appropriate mixtures or combinations of members of the above described classes may be treated, as desired.

The better drying a fatty oil is, the more suitable it is for my present process. I found that at least some of the fatty acids present in my oils should preferably contain more than one double bond in the molecule. This includes esters of the drying oil fatty acids and of the semi-drying oil fatty acids. I also found that esters of fatty acids having conjugated double bonds undergo easier my emulsion aggregation process, than fatty acids with isolated double bonds.

I have found that the fatty oils here above described are suitable to my emulsion-aggregation only if they have at least a certain critical minimum viscosity or body. In other words, to be susceptible to the aggregation in aqueous emulsion, they have to be pre-bodied by the usual means, known in the art. Such bodying may be carried out for instance by heating the oil to heat-bodying temperatures, or by blowing the oil with a gas, such as air or oxygen at room or elevated temperatures. Other means of bodying are treatment with ultra-violet light, by exposure to an electric field, etc.

I found that my oils have to have a minimum viscosity of Q in the Gardner scale, but preferably they should have still higher viscosities, such as V or Z-1 on the Gardner scale, and I further found that if the viscosity is more than Z-6, my emulsion aggregation reaction is still easier to perform.

However, drying oils are used in coating materials not only as such, but also in a blended form together with natural and synthetic resins.

The natural and synthetic resins, useful in my present process, are known in the art as varnish resins and all of them are soluble directly, or after a suitable treatment in varnish oils (i. e. oils used in varnish making).

As resin components of my air sensitive emulsions I may use many of the natural and synthetic resins, of which the following list are examples:

Cumar and indene resins,
Rosin,
Esters of rosin with polyhydric alcohols, (glycerine, glycols, pentaerythritol, sorbitol, mannitol, etc.)
Congo,
Congo esters,
Other copals (e. g. kauri), Maleic anhydride—rosin—polyhydric alcohol, type maleic resins,
Rosin modified phenolic resins,
So-called pure phenolic resins,
Terpene resins, etc.

In case oil-resin blends are used as the dispersed phase of my emulsions, the oils and resins may be advantageously cooked together in

the regular way as varnish solids are prepared in the varnish kettle. If in such a case unbodied oils are used as starting material, it is difficult to establish what the viscosity of the oil is in the varnish cook, as the oil could not regularly be separated from the resin with which it forms a uniform blend. In such a case we measure the viscosity of the oil-resin mixture and because such mixture may frequently be too viscous to be measured directly in the Gardner scale, when we refer to the viscosity of the blend, we may have to express same related to a solution of the blend in question in an organic solvent, such as for instance, in mineral spirits, giving also the solid content of such a solution.

As a general observation, I may mention that fatty oils form more readily air sensitive emulsions in presence of resins, than in absence of resins. In other words, if we compare cooks at the same temperature and for gradually progressing times of cooking, we find that cooks in which resins are present, form earlier air sensitive emulsions, under otherwise comparative conditions, than fatty oils alone in absence of resins. This statement is meant to apply for such cases in which emulsions of various cooking times are compared and checked whether under comparative reaction conditions they could be aggregated to the state in which they yield air sensitive emulsions. The resin containing cooks can be converted into air sensitive emulsions with a shorter cooking time than the resin-free comparative oil cooks.

TREATMENT CONDITIONS

BODYING

The first step in my process is, as indicated above, the bodying of the oil. This is effected in any of several known ways, such as:

1. By heating the oil, at suitable bodying temperatures, above 200° C., and usually above 250° C., until the desired viscosity is attained. (Stand oils, polymerized oils, or heat bodied oils.)

2. By blowing air, oxygen, or ozone over or through the oil to be thickened, either at room temperatures or at elevated temperatures. (Oxidized oils or air blown oils.)

3. By utilizing various gases, such as SO₂, H₂S, CO₂, N₂, etc., either to blanket the oil's during heat treatment or to treat the oils directly by blowing or bubbling the gas through the oil, either with or without the use of heat. (Non-oxidized bodied oils.)

4. By treating the oil with ultra-violet rays. (Uviol oils.)

5. By treating the oil in an electrical circuit with a potential difference capable of yielding bodying (Voltol oils.)

6. By bodying oils with modifying agents (polar compounds) as disclosed in my U. S. Patents Nos. 2,189,772; 2,213,944; 2,293,038; 2,298,270; 2,298,916; etc., and the various divisions and continuations thereof.

7. By heat-bodying under vacuum, occasionally coupled with a steam treatment to distill off free fatty acids.

Combinations of certain of these bodying techniques may be employed, as, for example, bodying with polar compounds in the presence of an electro-static field.

It is important to the attainment of best results that the oil should be bodied before emulsifying it and treating it in the emulsion in accordance with my invention. Even where the bodying is relatively slight some advantages may

be realized, but the strikingly improved results of my preferred method are most readily produced if the oil is quite heavily bodied. The extent or degree of bodying may vary over a considerable range, depending upon the purposes in view. However, in one preferred practice of the invention, the range of bodying desirable before emulsion aggregation may be defined by limits, as follows:

10 In the first place, the oil should be bodied at least to a degree such that when heated to 160° C. with 4½% sulfur an irreversible gel will form within about 4 hours and most desirably within about 3 hours.

15 On the other hand, the oil preferably should not have a body heavier than that which would result in conversion to an irreversible gel in less than 15 minutes when vulcanized with ½% sulfur at 120° C.

20 It may be mentioned that these limits, as just defined, are applicable not only to emulsion-aggregation treatment of fatty oils themselves but also to similar treatment of fatty oils in admixture with resins, thereby yielding emulsion-aggregated varnish solids of the oleo-resinous type.

I prefer to define the desired viscosity as above described, because, in the light of present knowledge, it is easier to apply some such test than it is to separate the component parts of an oleo-resinous mixture in order to determine the viscosity of the oil alone.

In addition to the foregoing limits of the range of bodying, it may be mentioned that alternatively the preferable range of bodying of the oil may be expressed by any suitable viscosity scale. Thus, e. g., for natural oils a satisfactory range of bodying is from about 15 to 20 poises (Y on the Gardner scale) up to in the neighborhood of 800 poises (beyond the upper limit of the Gardner scale). For most purposes it will be found desirable to utilize a viscosity upwards of about 100 poises. The measurement of the desired body by viscosity scales will, of course, be best suited to the situation where the oil is bodied prior to admixture with a resin, as in the preparation of varnish bases.

The best viscosity for any particular oil or oleo-resinous mixture will be a function of several variables. To mention a few, the solid content and pH of the emulsion used, the temperature of treatment, the type of resin used, if any, the nature of the oil, the proportion oil to resin, the effect desired, etc., will influence the degree of body to be employed. In each individual case, however, it is easy to determine the most favorable viscosity to use. After the proper viscosity has been determined, the desired conditions can readily be duplicated. For instance, one may simply note the appearance and the behavior of so much of the material as clings to the stirring paddle when it is lifted out of the kettle from time to time, such as flow and the length of the string formed, etc.

It should be remembered, of course, that different resins have diverse effects on the oil bodying. Allowances must be made for this fact in calculating the time necessary to attain proper bodying of a particular mixture, and it should also be realized that in a certain case it may be possible to proceed to the emulsion-aggregation treatment step before the viscosity of the mixture is as high as would be necessary in another case with a different oleo-resinous mix.

A further convenient method establishing the

necessary critical minimum viscosity of my fatty acid esters is the ammonia test, which is described in more detail further below in Example 32. The test comprises in immersing a small pill of the ester by the aid of a glass rod into concentrated ammonium hydroxide solution kept in a test tube. Satisfactory viscosity is reached if the pill solidifies in the concentrated ammonia in not more than 5 minutes to such an extent that when pressed against the wall of the test tube by the glass rod, it should feel rubbery (elastic), dry and should not stick to the wall of the test tube.

The ammonia test is particularly suitable to determine the necessary critical viscosity limit in the case of oil-resin mixtures or in the case of alkyd resins, which very often do not have a ready flow at room temperature. Alkyd resins, as it is known, are very viscous and often form plastic solids at room temperature, if the polybasic acid content is considerable.

It should be mentioned that generally speaking esters containing fatty acids with conjugated double bonds have a lower critical minimum viscosity requirement from point of view of the emulsion aggregation process, than similar esters with isolated double bonds.

AGGREGATION PROCESS

As described further above, it is a prerequisite to my process that the oils should have at least a certain critical minimum viscosity. If they reach that minimum viscosity, they may undergo the emulsion aggregation process.

My aggregating agent is oxygen. I believe that the active agent of my process is an electrically charged oxygen particle. However, I have no definite proof of that supposition. As not any and all oxygen may act in my process as aggregating agent, I shall refer the oxygen which is suitable in my process as "active oxygen" and I believe that the particles of this active oxygen are most probably electrically charged.

I can obtain my active oxygen in various ways.

(1) I may use a peroxide, such as a metal peroxide or hydrogen peroxide, or an organic peroxide to supply my active oxygen to my emulsions. (2) I may blow oxygen or an oxygen containing gas, such as air, through my emulsions. (3) I may use the oxygen which is present in the water phase of my emulsion as absorbed oxygen.

However, as the three kinds of oxygen above referred to do not act with equal velocity, auxiliary assistance may be needed in many of the cases.

I found for instance that the application of heat is accelerating the action of my aggregating agent (active oxygen). In fact, the application of heat is one of the roads which lead to activate the oxygen particles in my reaction. Temperatures above room temperature may be used for such activation and they should not exceed the boiling point of the emulsion to be treated. Usually temperatures between 50° C. and 80° C. are useful, but temperatures below 50° C. and above 80° C. may also be used, if other reaction conditions warrant such a procedure, but such temperatures should not exceed the boiling point of the aqueous dispersion.

Agitation of the emulsion also acts as an activating factor and it may advantageously be combined with the application of temperatures higher than room temperature. It is believed that the oxygen particles which are absorbed in the aqueous phase of the emulsion may obtain electric

charges by friction, caused by forced movement. Elevated temperatures themselves are increasing the movement of air particles absorbed in water and agitation causes also an increase in the movement of absorbed gas particles. The combination of agitation and heat causes increased and combined activation.

In case peroxides are used and oxygen is liberated in situ, further activation by agitation and/or heat is not a necessary requirement and the aggregation may be carried out in a satisfactory way, at room temperature and even at temperatures lower than room temperature. In case, however, only the oxygen present by natural absorption in the aqueous phase is used for the aggregation process, it is necessary to activate same and temperatures higher than room temperature and preferably agitation are needed to complete the reaction within practically useful time intervals.

If blowing of air or oxygen through the emulsion is used as a source of the aggregating active oxygen, the conditions are usually inbetween the above-mentioned two extremes, on one end of using peroxides and on the other end of using the oxygen absorbed in the water as sole aggregating agent. Whether heat and agitation should be used in connection with blowing air or oxygen through the emulsion, may depend on the particular reaction conditions involved, on the fineness of sub-dividing the gas bubbles used, the body and nature of the oil or oil-resin mixture, amongst others. It may be mentioned as a general rule, however, that under otherwise equal conditions peroxides act fastest, blowing of air or oxygen is next fast, and using the absorbed oxygen only, is the slowest of the three alternatives. Further, it may be stated that under any condition agitation and/or heat accelerate the action of the oxygen and that their use is essential only in the slowest range.

With regard to the quality of the film-forming solids, the films which have been produced by the smallest possible quantity of active oxygen are most desirable, as they contain very little chemical oxidation products, whereas in cases where peroxides are used in considerable proportions, the active oxygen may cause chemical oxidation, yielding by-products, which are in many cases undesirable components of films obtained from coating compositions.

CRITICAL PH CONCENTRATION

One of the important criterions of my process is the pH of the emulsion. I found that it is important to have critical pH limit to carry out my process satisfactorily. I found that the reaction is extremely slow with a pH of 7 and there is a very slow range from about a pH of 5.7 to about 8.4. The range is very active below 5.7, such as for instance in the neighborhood of pH of 2.8 and also above 8.4, for instance in the region of pH of 10.5 and higher. In other words, the reaction is greatly accelerated by a pH below 5.7 or above 8.4. However, for many purposes if working on the alkaline side I found it to be advantageous to have a pH of at least 10 and if working on the acid side, to have a pH which does not exceed 4.

It has been found that metallic driers are accelerating the emulsion aggregation process particularly in such cases in which the aggregation is carried out in an alkaline medium. Therefore, if metallic driers are desired to be present in the fatty oils, it is of advantage to work on the alka-

line side. However, if the absence of metallic driers is desired, a conversion in an emulsion on the acid side is more desirable. Further, it may be mentioned that conversion on the acid side is advantageous if a constant pH is desired. In case of emulsion aggregation on the alkaline side, the pH generally changes insofar as it gradually becomes lower.

CONCENTRATION OF THE EMULSION

I also found that the concentration of my emulsions, to be aggregated, is important and as a general rule lower solid content will accelerate the reaction, whereas higher solid content will retard same. A particularly advantageous range is between 10% and 20% solids. Vehicles of coating materials should preferably have solids in the neighborhood of 50% or more. It is possible to carry out the emulsion aggregation process in the neighborhood of 50%, or in other words, air sensitive emulsions can be produced in emulsions having 50% solids. In fact, even higher solids going up to 70% may be applied. However, the more concentrated emulsions we use, the more accelerating and activating conditions we have to apply for satisfactory results. For instance at a 20% concentration it is easy to apply the reaction using the absorbed oxygen only, as aggregating agent, with comparatively low temperatures and slow agitation. However, using higher concentrations it may become necessary to use peroxides as activating agents and if the concentration is still further increased, the simultaneous use of peroxides and heat and agitation may be required to secure the transformation desired.

It may be advantageous to carry out my process in an emulsion with low solid content, to accelerate the process and after the emulsion aggregation is completed, to concentrate the comparatively dilute emulsion. Such concentration may be carried out by any of the means known in the art in connection with concentrating emulsions, for instance, concentrating natural rubber latex. One example of such a method is electro-decantation.

OXYGEN SUPPLYING AGENTS

As mentioned further above, if other reaction conditions are proper, the oxygen content of the water, present in the emulsion, may be satisfactory.

Oxygen may be supplied to the emulsion in form of oxygen gas or oxygen containing gases, such as air, by bubbling through the emulsion such gases or by introducing them by known means. Ozone may also be used.

To produce oxygen in situ peroxides or other per-compounds may be used. In most of the examples hydrogen peroxide is used to illustrate the addition of per-compounds. However, other peroxides may also be used, such as sodium peroxide, barium peroxide, magnesium peroxide, zinc peroxide, other metal peroxides, or organic peroxides, such as benzoyl peroxide, urea peroxide, etc. Examples of per-compounds are further perborates, percarbonates, persulfates, such as potassium, sodium and ammonium persulfates, perchlorates, pyrophosphate peroxides, ozonides, etc. The criterion of the usefulness of these agents is that they should supply oxygen in situ under the reaction conditions applied in my process and that the emulsion could be prepared in such a way that it should not break in their presence.

EMULSIFYING AGENTS

Great variety of emulsifying agents may be used in my process. A list of such emulsifying agents is given, for instance, under the title of Surface-Active Agents in the January 1943 issue of Industrial and Engineering Chemistry, on pages 126 to 130.

Soaps of fatty acids are for instance satisfactory emulsifying agents. A list of some others is given herewith:

Trade Name and Source	Manufacturer's Description
15 Duponol ME, E. I. du Pont de Nemours & Co.	Fatty alcohol sulphate.
Aerosol OT, American Cyanamid Company.	Dioctyl ester of sodium sulphosuccinic acid.
Emulphor AG, General Dyestuff Corporation.	Polyethylenoxide condensation product.
20 Nekal A, General Dyestuff Corporation.	Sodium salt of alkylsubstituted naphthalene sulphonate.
Igepon, General Dyestuff Corporation.	Sodium sulphonate of an oleic acid ester of an aliphatic compound, for instance, of the type of $C_{17}H_{33}CON-CH_2C_6H_4SO_3Na$.
Triton, Rohm & Haas.	Sodium salt of aryl alkyl poly ether sulphonate.
25 Emulgor A, Glyco Products.	A highly polymerized glycol ester.
Wetanol, Glyco Products.	Modified sodium salts of sulphated fatty alcohols.
Darvan #1, R. T. Vanderbilt Company.	Polymerized sodium salts of alkyl naphthalene sulphonic acids.
30 Hornkem, Hornkem Corp.	Purified sulpholignin—.
Beta Sol, Onyx Oil & Chemical Company.	Quaternary ammonium salt.
Pentamul 126, Heyden Chemical Corp.	Pentaerythritol monooleate.
Pentamul 147, Heyden Chemical Corp.	Pentaerythritol monolaurate.

I have found that from the various emulsifying agents such types are most suitable, which are active both on the acid side and on the alkaline side. The non-ionic emulsifying agents belong to that class, such as for instance, Pentamul 126 and 147, nonaethyleneglycolmonooleate, or the corresponding dioleate, or the corresponding monolaurate or dilaurate or monoricinoleate or diricinoleate. (Glyco products.) A further satisfactory group is the one of the cation-active emulsifying agents. Examples are the quaternary ammonium salts. As will be seen, the fatty alcohol sulphates (for instance, Duponol ME) are also suitable for my process.

VACUUM

The application of vacuum, that is reducing the pressure over the emulsion, accelerates the emulsion aggregation process and helps to activate the oxygen particles present. This will be illustrated in the examples. (See Example 14.)

EXAMPLES

The examples given here below illustrate my process and my products. I do not intend, however, to limit my products and my process to the scope of the examples given.

In many of the examples it was decided to determine the state of the dispersed phase of the emulsions and the progress of the emulsion aggregation reaction by coagulating the emulsions or sample portions thereof. This was done by the addition of a saturated barium chloride solution, which coagulates the emulsions, for instance emulsions made with Duponol ME, with ease. The resulting coagulum contained the dispersed phase of the emulsion, together with a small percentage of the water.

The appearance and condition of the coagula

permits to classify same into one of the following classes:

1. FV, fluid and viscous.
2. HV-TP, Heavy, viscous but still showing fluidity in the entirety of the product at temperatures higher than room temperature but not exceeding 100° C.
3. IG-CF, intermediate stage, having slight gel structure, but still showing cold flow characteristics.
4. NT-ST, a non-thermoplastic gel, soft and having considerable tack (NT-ST, for non-thermoplastic, soft and tacky.)
5. GD, a gel stage, dry and free of tack.

The coagula were dried at elevated temperatures, to drive out any residue of water and the resulting solids were classified into one of the above designated classes.

In many of the examples here below, this classification was used to express the state of the dispersed phase of the emulsions.

In the examples following here below in many instances the nature of the process and its variables are demonstrated, instead of showing how to make a coating composition. For instance Examples 1 to 25 and 37 and 38 belong to this group, and also to a certain extent Examples 32, 33, and 39 to 50. It should be mentioned that in all these examples where at least stage 4 (a non-thermoplastic gel) has been reached, the emulsion is an air sensitive emulsion, which can be used itself as a coating composition or which may be used as a component of coating compositions. (Obviously, where stage 5 has been reached, the reaction is more advanced and the emulsions are suitable in coating compositions.)

Examples 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 39, 40, 41, 43, 45, 46-A, 46-B, 47, 48-A, 48-B, 48-C, 49, 50-A and 50-B, describe the preparation of coating compositions.

EXAMPLE 1

For a series of experiments a master batch emulsion was made, using OKO bodied linseed oil of the viscosity M-37. To 350 grams of the M-37 oil, 5 grams of concentrated ammonia were added. To 350 grams of distilled water, 5 grams of concentrated ammonia were added. The aqueous ammonia solution was gradually added to the oil under constant agitation, whereby a uniform emulsion was obtained. A further 700 grams of distilled water were then added to the emulsion, to produce an emulsion with 25 per cent solid content. The OKO M-37 oil is a specially vacuum bodied viscous oil, having a low acid number. The product used in this example is marketed by Spencer Kellogg & Sons, Inc., and had an acid number of 2.7. The pH of this solution was somewhat above 10. The ammonium hydroxide formed soap in situ with the fatty acids of the oil and this soap acted as emulsifying agent.

EXAMPLE 2

To 400 grams of the master batch emulsion of Example 1, 3 grams of 30 per cent strong hydrogen peroxide were added, together with 30 grams of distilled water. The hydrogen peroxide and distilled water were mixed first together. Then this mixture was added to the master batch emulsion. The emulsion was agitated slowly and heated to and maintained at 60° C. During the reaction the pH is usually dropping and therefore further small portions of concentrated ammonium hydroxide were added to keep the emul-

sion on the alkaline side and to preserve its stability. The agitation and heating of the emulsion was maintained for 2 hours, after which both the heating and the agitation were stopped overnight.

The next day the emulsion was reheated to 60° C. and agitated at that temperature for another 2 hours, after which period a further mixture of 3 grams of 30% hydrogen peroxide and 30 grams of distilled water were added. After this addition, the emulsion coagulated irreversibly and acetic acid was added to the emulsion, to acidify and to complete the coagulation. A sample of the coagulum was placed in a Petri dish and dried in an electrically heated oven at 130° C. In another Petri dish some untreated M-37 oil was heated in the same oven at the same temperature and for the same length of time. The dry product from the coagulated emulsion was a soft, non-thermoplastic gel, having a relatively low tensile strength and a somewhat darker color than the control M-37 oil. The untreated M-37 oil heated alongside the coagulum of the emulsion remained an oily product with a light color and ready flow. The treatment time in this particular example was 4 hours at 60° C. and another 16 hours standing at room temperature. The actual hydrogen peroxide quantity used was somewhat less than 1% during the treatment period, as at the addition of the second hydrogen peroxide quantity the emulsion coagulated. The emulsion had 100 grams of oil and 3 grams of 30% hydrogen peroxide solution was added, making the active hydrogen peroxide equivalent to 0.9%, based on the oil content.

It should be noted that under the reaction conditions of this example, using high alkalinity and elevated temperatures together with hydrogen peroxide, the transformation of the liquid M-37 oil is a rapid one and additional hydrogen peroxide addition coagulated the emulsion. During the reaction under the reaction conditions used in this example, quite considerable evaporation of water occurred and it was necessary to add distilled water from time to time to the emulsion, to maintain the original solid content, and to prevent the concentration of the emulsion.

It should be noted that the low solid content of the emulsion also added to the causes which secured rapidity of the aggregation process.

Presence of emulsifying agents, which are non-ionic or cation-active and work also in the acid region are needed to preserve the emulsion under the reaction conditions of this example and their absence may have caused the flocculation observed.

EXAMPLE 3

In this example 600 grams of the master batch emulsion of Example 1 were used, to which 10 grams of 30% hydrogen peroxide were added under agitation. As soon as the mixture was homogeneous, the agitation was stopped and the emulsion left standing at room temperature for 72 hours in a beaker, covered with a watch glass. After 72 hours had lapsed, the emulsion was coagulated by the aid of acetic acid. A portion of the coagulum was dried in an oven at 130° C. The resultant product was a non-thermoplastic gel similar to that obtained in Example 2, corresponding in our scale to Stage 4 (NT-ST). The quantity of hydrogen peroxide (assay) was 2% in this example, based on the oil content of the emulsion. It may be seen that even at room temperature, the M-37 oil is aggregated to an

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advanced stage at the pH of this example, but the time interval necessary for the conversion was longer than in the case of the comparative Example 2, in which elevated temperature was used. The solid content of this emulsion was also 25% and the quantity of hydrogen peroxide used was much more than in the case of the comparative Example 2.

EXAMPLE 4

100 grams of M-37 oil were emulsified with the aid of a colloid mill, using 2 grams of Duponol ME and 200 grams of distilled water. 3 grams of 30% strong hydrogen peroxide were added to the emulsion and the same was kept at room temperature in a beaker covered with a watch glass for 18 hours. The temperature of the emulsion was then raised to 60° C. and under constant agitation this temperature was maintained for 5 hours. The entire emulsion was coagulated then by the addition of a 5% strong barium chloride solution. A portion of the coagulum was dried at 130° C. and the product obtained was of oily nature, corresponding to stage 1 of our scale (FV). The above emulsion had a pH very slightly above 7, that is to say, it was very faintly alkaline, whereas the emulsion of Example 2, was much more alkaline. This example shows that the pH is very important for the preparation of air sensitive emulsions and that higher pH values are advantageous, if we consider the alkaline side of the pH scale alone. Duponol ME is a fatty alcohol sulphate, marketed by E. I. du Pont de Nemours & Co. That Duponol ME does not retard the aggregation process and is not the cause of the lack of conversion in the case of the present example, can be seen if we consider other examples in which the same agent was used and aggregation occurred readily. 0.9% hydrogen peroxide (assay) was used in this example, based on the oil content. The emulsion of this example had higher solids than the one used in Example 2.

EXAMPLE 5

100 grams of M-37 oil was emulsified by the aid of 0.4 grams of sodium hydroxide, dissolved in 200 grams of distilled water. The emulsion was treated for 4 days in such a way that during daytime the temperature of the emulsion was raised to 60° C. and emulsion was agitated, whereas at night time the temperature of the emulsion was room temperature and no agitation occurred. Altogether the emulsion was exposed to the elevated temperatures and agitation for 20 hours during the 4 days treatment period. At night time, the emulsion was kept in a glass beaker, covered by a watch glass. In total 12 grams of a 30% strong hydrogen peroxide solution were added in 4 equal installments during the 4 day period. After the fourth day, the emulsion so treated was completely coagulated by the aid of acetic acid and a portion of the coagulum was dried at 130° C., yielding a porous and fairly rigid, almost tackfree gel, corresponding to my class 5 (GD). The emulsifying agent in this example was sodium soap, which was formed in situ by the sodium hydroxide and the fatty acid content of the oil.

In this example the pH was highly on the alkaline side. The reason for the very advanced stage obtained in this example is the simultaneous use of comparatively low concentration, high pH, elevated temperatures, hydrogen peroxide, and a comparatively long reaction period.

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EXAMPLE 6

A master batch of emulsion was prepared by using 400 grams of M-37 oil and emulsifying same with 400 grams of distilled water and 20 grams of Emulphor ON, using a colloid mill for the dispersion process. Emulphor ON was used to obtain an acid stable emulsion, for tests described further below. This emulsifying agent was of a different type from Duponol ME and is marketed by General Dyestuff Corporation and is a polyethyleneoxide condensation product.

The solid content of this emulsion was 50%.

EXAMPLE 7

This example was designed to investigate the role of the pH in the aggregation reaction of M-37 oil in an aqueous emulsion. Several 100 gram portions of the master batch of Example 6 were taken and treated as follows:

7-A.—Nothing was added to this portion, the pH being approximately 6.

7-B.—To this portion 1.2 cc. of 10% strong sodium hydroxide solution were added to give a pH of approximately 9.

7-C.—To this portion 2.4 cc. of 10% strong sodium hydroxide solution were added, to yield a pH of approximately 11.

All three of the above emulsions were treated by adding twice 3 gram portions of a 30% strong hydrogen peroxide to the 100 cc. size emulsions, the 2 additions having been carried out on 2 successive days. The emulsions were kept at room temperature in beakers covered with watch glasses for 6 days. It was noted that the pH of all emulsions dropped by this time. All of the emulsions were coagulated with a 5% strong barium chloride solution and the coagula dried at 130° C., yielding in the case of Example 7-A, a viscous oil of the approximate range of stage 2 in our scale (HV-TP), whereas the product of 7-B was a non-thermoplastic gel, very soft and quite sticky, corresponding to stage 4 of my scale (NT-ST), and whereas the product of 7-C was a firm gel, having less tack and less softness, than the product of 7-B, and could be classified almost into Class 5 of my scale (GD).

It may be noted that under the conditions of this example an alkaline medium is necessary for the conversion by aggregation. It has to be considered, however, that in this example the emulsions were kept at room temperature, had a high solid content and were not agitated. It was interesting to see that increase in acidity occurred in all of the cases. The hydrogen peroxide content in these experiments was 3.6% based on 100 parts of oil.

EXAMPLE 8.—EFFECT OF FATTY ACIDS

170 grams of M-37 oil were mixed with 37 grams of linseed oil fatty acids and 10 grams of concentrated ammonium hydroxide. The whole was emulsified by adding 400 grams of distilled water. During this example, the pH was constantly maintained at around 9, by further additions of ammonium hydroxide. The emulsion was agitated, after it was heated to 80° C. The temperature and agitation were maintained for a total of 15 hours during a period of 72 hours. During the balance of the residual time, the emulsion was standing at room temperature in a loosely covered beaker. During the agitation period at elevated temperature at 4 occasions 6 gram portions each of 30% strong hydrogen peroxide were added to the emulsion in approximately equal intervals. At the end of the 72

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hours the emulsion was coagulated by adding barium chloride and a portion of the coagulum was dried at 130° C. The resulting product was a non-thermoplastic gel of a rather soft nature, corresponding to my stage 4 in my scale (NT-ST).

In this example it was seen that the addition of large quantities of fatty acids to the M-37 oil does not prevent the conversion of the oil by aggregation. This conclusion is, however, independent of the question of film quality, as fatty acids are not considered desirable in paints or varnishes.

EXAMPLES 9 TO 10.—EFFECT OF PROTECTIVE COLLOIDS

EXAMPLE 9

A master batch of emulsion was prepared, using 550 grams of M-37 oil and emulsifying same with 25 grams of 10% strong sodium hydroxide solution and 1,100 grams of distilled water. The emulsion so obtained was strongly on the alkaline side.

EXAMPLE 10

375 gram portions of the master batch emulsion of Example 9 were put into glass beakers and a concentrated solution of gelatin was added to each portion as follows:

10-A.—0.1% dry gelatin was added, based on the weight of the oil.

10-B.—1% gelatin was added based on the weight of the oil.

10-C.—5% gelatin was added, based on the weight of the oil.

To each portion, 1.6 grams of a 30% strong hydrogen peroxide solution was added, and the mixes were allowed to stand at room temperature for 96 hours. The emulsions were then coagulated and the coagula were dried in an oven at 130° C. The products of all 3 emulsions were very similar to each other and they were in the stage 4 in my scale (NT-ST). These emulsions were compared to a control emulsion 10-D having no gelatin, otherwise treated under similar conditions as the ones containing gelatin. The appearance of the dried coagulum of the control 10-D was similar to that of 10-A, 10-B, and 10-C, and therefore it may be concluded that the presence of gelatin does not appreciably influence the reaction, or in other words does not retard or accelerate the aggregation reaction.

EXAMPLE 11

This example was an exact duplicate of Example 10, and was run parallel with same, except using methyl-cellulose instead of gelatin. The results were quite similar to the ones obtained in Example 10, and showed that also methyl-cellulose has no marked effect on the emulsion aggregation process, either one way or the other way, under the reaction conditions here applied.

EXAMPLE 12

Two portions of the master batch emulsion of Example 9, 150 grams each, were taken and to one of them (Example 12-A) 1.5 grams of 30% strong hydrogen peroxide solution was added and to the other one (Example 12-B) 10 grams of the same 30% strong hydrogen peroxide solution. Both emulsions were kept at room temperature in loosely covered beakers for 96 hours. At the end of the 96 hour period, the emulsions were coagulated with barium chloride and the coagula

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dried in an oven at 130° C. Both coagula were non-thermoplastic gels being in-between stages 4 and 5 in my scale. It may be concluded from this experiment that under equal reaction conditions above a certain quantity of peroxide, a further increase in peroxide addition does not markedly change the product of the emulsion aggregation reaction.

EXAMPLE 13

In a 22 liter flask, 8,000 grams of linseed oil were bodied at 300° C., at a vacuum of 100 mm. Hg pressure, bubbling SO₂ gas through the oil at the rate of 20 grams an hour. After 3 hours of bodying 200 grams of the oil were taken out. The oil had a much lower viscosity than the M-37 oil used in the other examples, and the viscosity was in the neighborhood of Z in the Gardner scale. The 200 grams of oil were emulsified using 400 grams of distilled water and 8 grams of a 10% strong sodium hydroxide solution. The emulsion was heated to 70° C. and agitated at that temperature for a total of 32 hours, during a period of 1 week. In the rest of the time, the emulsion was kept at room temperature, was not agitated and was covered by a watch glass overnight. During the 32 hours heating period 40 grams of a 30% strong hydrogen peroxide solution were added at approximately equal intervals using equal portions. The emulsion had 33½% solid content and the total quantity of hydrogen peroxide added was 6% based on the oil content. At the end of the week the emulsion was coagulated, using acetic acid as coagulating agent and the coagulum was dried at 135° C. at the vacuum of 100 mm. Hg pressure. The product obtained was a soft, non-thermoplastic gel, in range of my stage 4 in my scale (NT-ST).

This example has shown that much less viscous oils can form air sensitive emulsions than M-37 oil.

EXAMPLE 14.—EFFECT OF VACUUM

M-37 oil was emulsified with distilled water and sodium hydroxide, using 0.45% sodium hydroxide on 100 parts of oil (parts by weight) and the emulsion was prepared in a way to yield 33% solid content. No peroxide was added. The emulsion was strongly on the alkaline side. A part of this emulsion (Example 14-A) was placed in a glass tube in such a way that ½ of the tube was filled with the emulsion and ½ was air space over the emulsion. The tube was connected with a vacuum pump and a vacuum was produced in the tube with a pressure of about 50 mm. Hg. pressure. The tube was then sealed. The emulsion was maintained at room temperature for 5 days after which it was opened. The main portion of the emulsion (Example 14-B) was kept as a control in a beaker covered by a watch glass and therefore being in constant control with the atmosphere. After the 5 day period lapsed, both emulsions were coagulated with barium chloride. The oil in the vacuum tube was almost a solid gel and was definitely in a more advanced conversion stage than the control, which was kept in the beaker. It seems, therefore, that reduction in the pressure is accelerating the conversion.

COMPARATIVE EXAMPLES 15 TO 24

EXAMPLE 15.—MASTER BATCH

In these comparative experiments a very heavily bodied linseed oil was used, which is known in the art as OKO M-37 oil. This product is ob-

tained by bodying linseed oil under vacuum, has a viscosity of approximately 800 poises and has a low acid value. As emulsifying agent 1% of Duponol ME dry was used, based on the weight of the oil to be emulsified. Distilled water was used as dispersion medium and the emulsion had a solid content of 20% by weight. The emulsion was made by adding a 10% solution of the Duponol ME to the oil and adding the water in small portions under agitation, until a uniform emulsion resulted before the addition of the next increment of the water. The emulsions so obtained showed satisfactory stability both in the acid and in the alkaline regions of varied pH values.

The emulsions were stirred by slow speed agitators at a temperature of 60° to 65° C. 500 grams of the emulsion were used in two-liter beakers. The beakers were covered, as much as possible, even if not air-tight, to prevent excessive evaporation and what evaporation still did occur, was compensated for by small additions of water from time to time.

EXAMPLES 16 TO 18.—FIRST SERIES

Variation of pH without peroxide addition

It has been found that the hydrogen ion concentration has a paramountly important role in the conversion process yielding air sensitive emulsions. Studies were made in a wide range of hydrogen ion concentration. In the alkaline region phosphate buffers were used to retard the decrease in pH value, which may be noted in these emulsion aggregation experiments carried out on the alkaline side. The examples in the acid region contained phthalates as buffers.

The following preparations were made to produce emulsions with various pH values on the alkaline side:

EXAMPLE 16

To 3,000 grams of the master batch emulsion of Example 15, 43 grams $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ was added as buffer. To vary the pH, the following preparations were made:

Example 16-A.—500 grams emulsion of Example 16, without additions, pH 8.4.

Example 16-B.—500 grams emulsion of Example 16, plus 10 grams of a 1% NaOH solution, pH 9.4.

Example 16-C.—500 grams emulsion of Example 16, plus 20 grams of 1% NaOH solution, pH 10.4.

Example 16-D.—500 grams emulsion of Example 16, plus 30 grams of a 1% NaOH solution, pH 10.8.

Example 16-E.—500 grams emulsion of Example 16, plus 40 grams of 1% NaOH solution, pH 11.1.

Further, the following preparations were made to produce emulsions with various pH values on the acid side:

EXAMPLE 17

3,000 grams of the master batch emulsion of Example 15 were prepared in such a way that it should contain the reaction product of 14.8 grams of phthalic anhydride and 2.0 grams NaOH, 1.2 times, dissolved in water. The emulsion so prepared had a pH of 2.8. The following preparations were made with this batch:

Example 17-A.—500 grams of the emulsion of Example 17, unchanged, pH 2.8.

Example 17-B.—500 grams of emulsion of Example 17, plus 0.8 gram NaOH, pH 4.8.

Example 17-C.—500 grams of emulsion of Example 17, plus 1.0 gram NaOH, pH 5.7.

EXAMPLE 18

A similar emulsion to the one of Example 15 was prepared directly to yield a pH of 7.1. 200 grams of M-37 oil, 20 grams of a 10% Duponol ME solution, 5.5 grams of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 780 grams of water, and 1.2 grams NaOH were used in preparing the emulsion, pH 7.1.

All the emulsions were heated to 60°–65° C. and kept at that temperature continuously for 96 hours, under constant agitation of approximately 45 R. P. M. Samples were taken out from the emulsions at various intervals and the same were coagulated to check the progress of the reaction.

The strongest degree of conversion was noted in the region of an initial pH above 10. Decided progress of the conversion reaction was noted in the pH region of 8.4 to 9.4, but the rate of conversion was considerably slower than the rate of the group with pH above 10.

The Examples have further shown that conversion at a pH of 7 was practically nil and at a pH of 5.7 was slow. It seems that there is a very ineffective region between a pH of 5.7 and 8.4 or in their neighborhood.

At a pH of 2.8 the conversion has a rapidity, which is comparable to the rate of conversion of the alkaline region in the neighborhood of a pH of 10.5.

To give a few details, it should be mentioned that the emulsion with pH 2.8 reached after 16 hours a stage which was almost 4 on our scale (NT-ST), and was in-between stages 4 and 5 after 96 hours. Whereas the emulsion with pH 7.1 was after 40 hours in stage 1 and reached after 96 hours a point below stage 3. In the conversion on the alkaline side the 3 emulsions above pH 10 reached stage 4 (NT-ST), in about 24 hours and were in-between stages 4 and 5 at the end of 96 hours. Whereas the emulsion with pH 8.4 reached stage 2 (HV-TP) in 24 hours and after 96 hours reached almost stage 4 (NT-ST).

Whereas the pH of all of the emulsions on the alkaline side dropped considerably during the progress of the reaction, the pH of the emulsions on the acid side remained fairly constant.

It should be emphasized that to none of the emulsions dealt with in this series was any peroxide or per-compound added.

EXAMPLE 19.—SECOND SERIES

Addition of peroxide

In this series 500 gram lots of the master batch emulsion of Example 15 were used and the pH in each case adjusted by addition of NaOH to be 12.2. The pH values after 24 hours were between 10.2 and 10.5, with the pH being lower in the case of higher peroxide additions. Four examples were made, with various quantities of hydrogen peroxide addition.

Example 19-A.—No peroxide.

Example 19-B.—½% of hydrogen peroxide based on the oil (1.7 grams 30% hydrogen peroxide).

Example 19-C.—1% of hydrogen peroxide based on the oil (3.3 grams 30% hydrogen peroxide).

Example 19-D.—2½% of hydrogen peroxide based on the oil (6.7 grams 30% hydrogen peroxide).

All 500 gram lots of Examples 19-A, B, C, and D, were heated to 60° C. and kept there for 14 hours, under agitation. Samples were taken out

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after 6 hours and at the end of the 14 hour period.

In all cases the pH dropped during the reaction period.

Increase in the peroxide quantity accelerated the progress of the reaction. After 6 hours, for instance, the control of Example 19-A was in stage 2 (HV-TP) whereas Example 19-B reached already stage 4 (NT-ST). After the 14 hours the control 19-A reached stage 3 (IG-CF), 19-B reached stage 4, 19-D reached almost stage 5, and 19-C was in-between 19-D and 19-B.

The results of this series are shown in Table A.

TABLE A

Ex-ample	Per cent H ₂ O ₂ ¹	6 hours ²	14 hours ³
19-A..	None	(HV-TP).....	(IG-CF) to (NT-ST).
19-B..	0.5	(HV-TP).....	(NT-ST).
19-C..	1.0	(IG-CF) to (NT-ST)...	(NT-ST) to (GD).
19-D..	2.5	(NT-ST).....	(GD).

NOTES

¹ Per cent H₂O₂ based on oil content.

² This column shows the condition of the coagulum after 6 hours treatment at 60° C.

³ This column designates the condition of the coagulum after 14 hours treatment at 60° C.

GENERAL REMARK

Expression (IG-CF) to (NT-ST) means that the product was inbetween the two stages here recorded.

From the above table, it can be seen that under the reaction conditions of these series, ½% of hydrogen peroxide has a slight effect in accelerating the aggregation process and that 1% and 2½% hydrogen peroxide correspondingly increase the acceleration of the emulsion aggregation. In all experiments in this series, the hydrogen peroxide was added initially.

EXAMPLE 20.—THIRD SERIES

Adding H₂O₂ in various ways

In this example, the same master batch was used as in the comparative experiments of Ex-

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20-C, were kept under agitation for altogether 20 hours, after which period all 3 were coagulated and were found to be in stage (NT-ST).

The conclusion to be drawn from these comparative examples is, that the variation in the manner in which 2½% of hydrogen peroxide was added before, during, or after, the first 5 hour period of processing, does not change the end result, if processing continues for at least 15 more hours, to make a total processing time of 20 hours and the reaction conditions are as here described.

EXAMPLE 21.—FOURTH SERIES

Effect of the solid content of the emulsion

An emulsion having 10% solids was compared with emulsions of 20%, 33% and 50% solids, under otherwise equal conditions and using an active pH range. No peroxide was used in this series, but agitation, heat and a favorable pH concentration were maintained.

To 1500 grams M-37 oil 150 grams of a 10% Duponol ME water solution was added under constant agitation. In 1305 grams distilled water 45 grams of 10% strong water solution of NaOH was added and this solution was gradually stirred into the oil containing the Duponol ME. The emulsion so prepared was used in the following concentration study:

Example 21-A.—1000 grams Example 21, as is, 50% solids.

Example 21-B.—666 grams Example 21, diluted with 334 grams distilled water, 33% solids.

Example 21-C.—400 grams Example 21, diluted with 600 grams distilled water, 20% solids.

Example 21-D.—200 grams Example 21, diluted with 800 grams distilled water, 10% solids.

The 4 emulsions were kept without any peroxide addition for 96 hours at 65° C., under agitation of about 45 R. P. M. Sample portions were coagulated after 24 hours, 72 hours and 96 hours treatment. The results together with the pH values were as follows:

TABLE B

Example	Original pH	After 24 hrs.		After 72 hrs.		After 96 hrs.	
		Coagulum	pH	Coagulum	pH	Coagulum	pH
21-A.....	11.9	1-2 (FV) to (HV-TP).....	10.3	2-3 (HV-TP).....	9.5	As before.....	9.6
21-B.....	11.7	Almost 2 (HV-TP).....	10.3	3 (IG-CF).....	9.6	Almost 4 (NT-ST).....	9.5
21-C.....	11.6	Almost 2 (HV-TP).....	10.5	Almost 4 (NT-ST).....	9.5	4 (NT-ST).....	9.4
21-D.....	11.4	2 (HV-TP).....	10.1	Better than 4 (NT-ST).....	9.0	4-5 (NT-ST) to (GD).....	9.0

ample 19. To 500 cc. of the master batch emulsion satisfactory quantity of sodium hydroxide was added to yield an initial pH of 11.5. The quantity needed was 0.23 gram of sodium hydroxide. Three 500 cc. batches were so prepared, all having the same constitution and the same pH.

20-A.—To the first of the 3 emulsions, 2½% of hydrogen peroxide was added at the start. The batch was then agitated.

20-B.—In this example, agitation started the same time as in the case of A, but the 2½% hydrogen peroxide was added in small portions over a period of 5 hours, to the batch.

20-C.—This was a comparative experiment to A and B and in this instance the 2½% hydrogen peroxide was added after the first 5 hour period lapsed.

All three products, that is, 20-A, 20-B, and

The results show that the conversion is greatly accelerated in the case of the emulsion having 10% solids, when compared to the emulsion having 50% solids. The others were inbetween these extremes.

EXAMPLE 22.—FIFTH SERIES

Effect of temperature

An emulsion was prepared containing 400 grams M-37 oil, 40 grams 10% Duponol ME water solution, 12 grams 10% NaOH solution, and distilled water to bring the emulsion to 10% solids, having pH of 12.2. Three lots of this emulsion, 500 grams each, were kept all under constant agitation for 120 hours at varying temperatures, as follows:

Example 22-A.—At room temperature of 23° C.

Example 22-B.—At a temperature of 38° C.

Example 22-C.—At a temperature of 50° C.

Samples were coagulated after 48 hours, 72 hours and 120 hours. The results were as follows:

TABLE C

Example	After 48 hours		After 72 hours		After 120 hours, Coagulum
	Coagulum	pH	Coagulum	pH	
22-A.....	2 (HV-TP).....	10.6	2 (HV-TP)....	10.0	2 (HV-TP).
22-B.....	2 (HV-TP).....	10.3	2 (HV-TP)....	9.8	4 (NT-ST).
22-C.....	3-4 (IG-CF) to (NT-ST)....	10.0	4 (NT-ST)....	9.6	5 (GD).

This example shows that increase in temperature accelerates the emulsion aggregation process, caused by active oxygen.

EXAMPLE 23.—SIXTH SERIES

Peroxide vs. no peroxide at varying pH values

Six portions of the master batch emulsion used in the 19 series, were used in this comparative series. The following were the individual characteristics of the six examples:

23-A.—This batch was acidified and buffered with sodium acid phthalate. The pH was adjusted to 2.8.

23-B.—Acidified and buffered with sodium acid phthalate, adding 2½% of hydrogen peroxide based on the oil content of emulsion. The pH of this example was also adjusted to 2.8.

23-C.—Acidified with sodium acid phthalate and pH adjusted to 5.7.

23-D.—Acidified with sodium acid phthalate and treated with 2½% hydrogen peroxide, based on the oil content. The pH of this example was also adjusted to 5.7.

23-E.—This batch was rendered approximately neutral with mono-sodium phosphate.

23-F.—This batch was rendered approximately neutral with mono-sodium phosphate and treated with 2½% of hydrogen peroxide, based on the oil content.

In the above 6 experiments, there are actually 3 parallel experiments, investigating at various pH ranges differences if hydrogen peroxide is used or eliminated. The total treatment time at 60° to 65° C. in each case was 96 hours and sample quantities of each emulsion were coagulated after 16 hours, 40 hours, and 96 hours in each of the 6 individual cases. The following table summarizes the readings.

TABLE D

Example	Per cent H ₂ O ₂	pH	After 16 hr. treatment	After 40 hr. treatment	After 96 hr. treatment
23-A.....	None	2.8	(IG-CF) to (NT-ST)....	(NT-ST)....	(NT-ST) to (GD).
23-B.....	2.5	2.8	(NT-ST).....	(NT-ST)+	(GD).
23-C.....	None	5.7	(FV).....	(HV-TP)....	Almost (NT-ST).
23-D.....	2.5	5.7	(FV).....	(HV-TP)....	(NT-ST).
23-E.....	None	7.2	(FV).....	(FV).....	(IG-CF) to (NT-ST).
23-F.....	2.5	7.1	(FV).....	(IG-CF)....	(NT-ST).

The 6 examples of this comparative series show the following conclusions: In the acid region the transformation is very slow near the neutrality point, fairly slow around the pH of 5.7, and somewhat faster at the pH of 2.8. Near the neutrality point around the pH of 7.2 the addition of hydrogen peroxide does not accelerate the conversion to a great extent. The presence of hydrogen peroxide does not show appreciable results at a pH of 5.7 either. However, at the pH range of 2.8, the addition of hydrogen peroxide is definitely accelerating the conversion. These results should be compared with the comparative examples of the series of Example 19, and it is interesting to consider Example 19-D, where

2½% of hydrogen peroxide was added at a pH of 12.2, together with 16-E.

The results permit the generalization that the hydrogen ion concentration is of primary importance and only where the hydrogen ion concentration is favorable can the right effect of hydrogen peroxide be noted. These conclusions obviously have to be limited to the actual reaction conditions used in these examples.

EXAMPLE 24.—SEVENTH SERIES

Effect of closed full containers in absence of agitation and absence of peroxides

With the master batch emulsion of Example 15, several comparative experiments were made at various pH ranges, to see whether conversion in closed bottles, which were full and were not agitated, having no free air space above the liquid and not using any addition of a peroxide or other per-compound, occurs or not. The results obtained show that even when an active pH range was used, the conversion was very slow and did never progress beyond the stage of (IG-CF).

EXAMPLE 25.—CONVERSION OF A MEDIUM VISCOUS OIL

In this emulsion medium heavy, SO₂-bodied linseed oil was used, made according to the method described in Example 13. It had a viscosity in the neighborhood of Z in the Gardner scale. Solid content of the emulsion was 33%. The emulsification was obtained by the aid of 0.4% sodium hydroxide, which formed soap with the free fatty acids of the oil. 6.5% of hydrogen peroxide was added (50% strong)—(about 2% assay, based on the oil). The emulsion was agitated for 32 hours, while maintaining a reaction temperature of 70° C. After coagulation and drying the product obtained was a non-thermo-

plastic gel, inbetween the stages of (NT-ST) and (GD). This example shows that less viscous oils than the M-37 oil may be well converted according to the present process.

EXAMPLE 26.—AIR SENSITIVE EMULSION CONTAINING SULPHUR

This example shows that an air sensitive emulsion may be prepared in the presence of large quantities of sulphur. The product of this example has been prepared in three steps.

1. Preparation of oil emulsion

100 grams of linseed oil bodied at 300° C. under vacuum while bubbling SO₂ gas through the oil,

(see Example 13) and having a viscosity of about Z-6 in the Gardner scale, was mixed together at room temperature with 2 grams of Emulphor AG. 100 grams of distilled water, 4 grams of a 10% strong water solution of Duponol ME and 3 grams of a 10% sodium hydroxide solution were mixed together. The latter water solution was then added to the oil under vigorous agitation. The resulting mixture was a viscous oil-in-water emulsion of approximately 50% solid content.

II. Dispersion of sulphur paste

32 grams of sulphur, 15 grams of magnesium silicate (Asbestine), 4 grams of mercaptobenzothiazol and 2 grams of Vandex (R. T. Vanderbilt Co.) (which is metallic selenium powder used as vulcanization accelerator) were mixed together with a solution consisting of 41 grams of water, 2 grams of Darvan (R. T. Vanderbilt Co.) and 14 grams of a 15% strong water solution of casein. The resulting mixture was ground on a paint mill and contained approximately 50% solids.

III. Preparation of product, useful for bristle setting

40 grams of oil emulsion I, and 57 grams of paste dispersion II, were mixed. The resulting mixture was stable in a closed bottle but coagulated as soon as it was exposed to the air in a thin film, having strongly air sensitive qualities. The above product had the following final formulation:

OVERALL FORMULATION OF #223-T-B

	Grams
SO ₂ -linseed-oil, visc. Z-6	100
Emulphor AG	2
Duponol ME (10% strong solution)	4
NaOH (10% strong solution)	6
Sulfur	83
Asbestine	39
Captax	10
Vandex	5
Darvan	5
Casein solution (15% strong)	36
Distilled water	206

EXAMPLE 27.—ADHESIVE TYPE COMPOSITION

140 grams raw linseed oil and 60 grams of WW wood rosin were heated to 300° C. in a slow process, reaching this temperature in about 95 minutes. The reaction mixture was held at 300° C. for 145 minutes. It was then cooled to room temperature. Next morning the mixture was heated to 250° C. in about 50 minutes, cooled to 150° C. at which temperature 35 cc. of varnish makers and painters' naphtha was added to the mixture. 100 grams of the resulting solution were dispersed in the following manner. First, to the solution 2 grams of Emulphor AG and 1.5 grams of oleic acid were added. Then a mixture was prepared of 25 grams of distilled water, 0.5 grams of Duponol ME dry and 1 gram of concentrated ammonium hydroxide (26° Bé). The two mixtures were then mixed together and passed through a three-roller-type laboratory paint mill. After the milling operation a further 8.5 grams of water and 5 grams of concentrated ammonium hydroxide (26 Bé.) were added to the dispersion. The resulting dispersion is useful as an adhesive and has strongly air sensitive properties, coagulating very readily in thin

films as soon as exposed to the action of air. It may be used also in admixture with pigments or better, pigment dispersions, such as calcium carbonate dispersion or a zinc oxide dispersion. If a small quantity of this emulsion is rubbed between 2 fingers, it coagulates to a solid film within a few seconds and usually in a shorter time than 1 minute.

EXAMPLES 28 TO 30.—PREPARATION OF PAINTS

The preparation of paints from air sensitive emulsions may occur according to two basically different processes.

1. The pigment may be ground into the vehicle solids before emulsification and
2. The pigments may be ground into the ready-made emulsions.

Generally speaking, the first method is more difficult to apply, because vehicle solids containing pigments are more difficult to emulsify, than the same vehicle solids, which do not contain pigment. In case the pigments are dispersed in the vehicle solids before emulsification, it may be often found advantageous to have some organic volatile solvents present in the vehicle, to facilitate grinding operations. It should be mentioned, however, that if the pigments are dispersed in the vehicle solids before emulsification, certain special effects may be obtained. For instance, the gloss in the final film may improve and further the emulsion aggregation may yield products with different characteristics in presence of pigments. Further, there may be differences in the way how the vehicle solids surround and coat the individual pigment particles in the two different cases of pigmentation methods.

Here below a few examples will be given.

EXAMPLE 28

Into 396 grams of M-37 linseed oil, 104 grams of red lead paste were mixed in, which paste contained 93% red lead and 7% linseed oil. Driers were added in the form of naphthenate driers yielding 0.1% lead, 0.03% cobalt, and 0.05% zinc as a metal, based on the oil content. The mixture was passed through a laboratory paint mill to form a uniform mixture.

To 100 grams of the above mix, 1 cc. of oleic acid were added, together with 10 grams of a 10% strong solution of Duponol ME dry in water. To this mixture 90 grams of water and 3 grams of 25% strong sodium hydroxide solution were added under agitation, to form an oil-in-water emulsion. The pH of the emulsion was 11. 5 grams of hydrogen peroxide, 30% strong were added to the emulsion. 24 hours after the hydrogen peroxide addition a film was tested and the emulsion yielded within 30 minutes a dry film, when applied with a Bird film applicator, depositing 0.0015" thick wet film. The pigment in this emulsion was 25% by weight, based on the vehicle solids.

EXAMPLE 29

200 grams of M-37 oil and 200 grams of titanium dioxide were milled on a laboratory paint mill to form a paste. 75 parts by weight of M-37 oil was mixed with 50 parts by weight of the paste here before described. 20 parts of mineral spirits were added, together with driers yielding 0.1% lead, 0.03% cobalt, and 0.05% zinc on the oil content. To 100 grams of the above mixture, 1 cc. of oleic acid were added, together with 10 grams of a 10% strong Duponol ME solution. Into this

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mixture 90 grams of water and 3 grams of 25% sodium hydroxide solution were added slowly under agitation, to yield an emulsion of the oil-in-water type with a pH of 10.9. During 15 minutes 4 grams of hydrogen peroxide (30%) were added, and the emulsion yielded fast drying paint films after a 24 hour storage period, at room temperature.

EXAMPLE 30

100 grams of M-37 oil and 100 grams of ester gum were melted together at low temperature and 40 grams mineral spirits were added to the mixture, together with driers, yielding 0.1% lead, 0.03% cobalt, and 0.05% zinc, as metal, based on the oil content. Further 10 grams of linseed oil fatty acids were added to the mixture, which was then emulsified by 220 grams of water and 20 grams of concentrated ammonium hydroxide. The pH of the emulsion was 10. Five grams of hydrogen peroxide, 30% strong, was added to the emulsion. To 200 grams of this emulsion 5 grams of concentrated ammonium hydroxide were added, together with 100 grams of a 5% strong methyl-cellulose solution (4000 cps.) and 110 grams of water. After this dilution of the emulsion, the following pigments were stirred into same: 32 grams of titanium dioxide rutile type, 411 grams of lithopone, and 80 grams of China clay (Dawson clay). The mixture was passed once through a laboratory three-roller paint mill and formed a fast-drying flat paint. A film deposited by the aid of a B'rd film applicator, yielding 0.003" thick wet film yielded a film which was in stage A within 1 hour, as measured by the drying standards according to the Official Digest of the Federation of Paint and Varnish Production Clubs, No. 221, December, 1942, page 553.

EXAMPLE 31.—PREPARATION OF A FLAT WALL PAINT

500 grams of ester gum and 500 grams of M-37 oil were melted together at low temperature until they formed a uniform melt. 200 grams of mineral spirits were added to the mixture, together with driers amounting to 0.1% of lead, 0.03% cobalt and 0.05% zinc, all as metals, based on the oil content.

To 300 grams of the above varnish, 30 grams of a 10% strong solution of Duponol ME dry in water were added under agitation. A mixture of 270 grams of water and 2 cc. of concentrated NH_4OH was prepared and the water was slowly added to the varnish mixture under agitation. The resulting emulsion had a pH of 8.9.

The pH of the emulsion was brought to 9.5 by the addition of 2 cc. of concentrated ammonia. 15 cc. of a 30% strong hydrogen peroxide solution was then added to the emulsion slowly. The pH of the mixture dropped somewhat and therefore a further 5 cc. of concentrated ammonia were added to the emulsion to keep same considerably on the alkaline side. 300 grams of a 5% strong water solution of methyl cellulose (4000 cps.) and 230 grams of water were added to the above emulsion. Under stirring by hand, the following pigments were mixed into the diluted emulsion:

96 grams of titanium dioxide, rutile type, 1,233 lithopone, and

240 grams China clay, known as Dawson clay.

The mixture was passed through a loose laboratory type three-roller paint mill, and a smooth paste paint resulted, which could be diluted with water in the proportion of about 2 parts of paste

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paint per volume to 1 part of water per volume, to yield a good brushing flat white wall paint of good quality.

EXAMPLE 32.—COMPARATIVE SERIES OF VARNISH BASES, WITH VARIOUS RESINS, VARYING VISCOSITIES, AND COOKING TIMES, AND VARYING ADDITION OF HYDROGEN PEROXIDE

Ammonia test

In this series an unbodied linseed oil was used as oil ingredient, containing beta-methyl anthraquinone as bodying accelerator, in small quantities. As resin ingredients, three different resins were used in the comparative examples. The resins were typical for each of three types of varnish resins, popular in the varnish trade. The first one was an ester gum, having an acid number of 8 to 10, the second resin was a maleic type resin, obtained by condensation of rosin, maleic anhydride and glycerine. The particular resin used was Arochem 520, marketed by Stroock & Wittenberg Corp. The third resin was a rosin and polyhydric alcohol modified phenol-formaldehyde type resin, marketed by the Paramet Corporation under the trade name of Paranol 1750. With each of the three resins, three different varnishes were cooked, which varnishes had different oil lengths. With each resin a 50 gallon long, a 25 gallon long, and a 12½ gallon long varnish was cooked. The cooking temperature of the varnishes was 290° C. and sample batches were taken out from the cooks at intervals running from 30 minutes up to 3 hours and 30 minutes in some of the cases. Obviously, with many of the varnishes, the cooks had to be terminated much earlier, because of the high bodying speed, of the varnish base and in the cases of the cooks with Arochem 520 the cooking temperature had to be reduced to 260° C. Even that way the 50 gallon long cook could not be cooked longer than 2 hours and the 12½ gallon cook was cooked for 1½ hours only. In the case of the 12½ gallon Paranol 1750 varnish the maximum cooking time was only 60 minutes at 290° C.

As most of the varnish bases had very heavy viscosity and some of them were solids at room temperature, it would be difficult to express the viscosity of the various cooks in the Gardner scale. Therefore, a small portion of these varnish bases was thinned down with mineral spirits to 50% solids, and viscosity readings were made on these mineral spirits solutions, to find a proper expression of their viscosity.

In case of the ester gum the various samples of diversified cooking time in 50 gallon length yielded viscosities from A to F in the Gardner scale, whereas in 25 gallon length the viscosity was from A to J, and at 12½ gallon length they were from A to B.

In case of the maleic type resin, the viscosities of the 50 gallon length ranged from B to I, at 25 gallon length from B to T, and at 12½ gallon length from A to H.

In the case of the 50 gallon modified phenolic resin varnish the viscosities ranged from B to I and in the same type of varnish at 25 gallon lengths from C to H, and at 12½ gallon lengths from F to H.

Before going into the details of the behavior of the various cooks herein referred to, it should be mentioned that a test was found to express the satisfactory degree of bodying of oils in the presence or absence of resins, in making air sensitive emulsions with ease. The test consists

of immersing by the aid of a glass rod a drop of the varnish base into concentrated ammonia. If the immersed pill solidifies and forms a dry and non-sticky product within a time not exceeding 5 minutes from the time the immersion started, the body is satisfactory. This test can be easily carried out in a test tube and by rubbing the pill by the aid of the glass rod against the wall of the test tube, its solidity and stickiness can easily be established. This test works satisfactorily in most cases and the exceptions are such products, which form at room temperature a solid pill because of their resin content at any period of the cooking.

A few examples of ammonia test data were as follows:

TABLE E
[Maleic resin 50 gal. length]

Cooking time at 260° C., in minutes	Viscosity at 50% solids Min. Spirits	Ammonia Test
90.....	E.....	Negative.
120.....	F.....	Slightly Positive.
150.....	U-V.....	Positive.

¹ Gardner Scale.

TABLE F
[Ester gum 50 gal. length]

Cooking time at 295° C., in minutes	Viscosity at 50% solids Min. Spirits	Ammonia Test
65.....	C.....	Negative.
115.....	L.....	Almost Positive.
130.....	O.....	Positive.

TABLE G
[Modified phenolic resin 50 gal. length]

Cooking time at 295° C., in minutes	Viscosity at 50% solids Min. Spirits	Ammonia Test
75.....	K.....	Almost Positive.
90.....	M.....	Positive.

In 25 gal. length, cooked at 295° C., the ester gum gave positive ammonia test after 4 hours and 35" at a 50% solids viscosity of I. The corresponding figures for the maleic resin were: (270° C.) 1 hr. 45', Visc. R. and for the modified phenolic resin: (295° C.) 1 hr. 25', Visc. N.

As it will be seen, when the ammonia test is positive, the air sensitive emulsion formation goes with great ease. However, air sensitive emulsions may be prepared with shorter cooks than the ones yielding a positive ammonia test.

From the above varnish cooks emulsions were prepared by a uniform method of emulsification. The method used was as follows: 100 grams of the varnish base were heated to a temperature at which it was readily fluid. Driers were added and mixed into the varnish base. The drier combination used was 0.5% lead, 0.03% cobalt and 0.02% manganese, based on the oil content, of the varnish base. To the warm varnish base, 10 grams of a 10% strong water solution of Duponol ME dry were added. Then a mixture was prepared from 90 cc. of water and 1 cc. of a 10% strong sodium hydroxide solution in water. The water was heated to almost boiling and the sodium hydroxide containing water was gradually stirred into the varnish base, containing the Duponol solution. After 24 hours, the pH of the

emulsion was taken and a 10% strong solution of sodium hydroxide was added to the emulsion to bring the pH to 9.5, (plus-minus ½ pH degree). Half cc. quantities of hydrogen peroxide, 30% strong, was added to the emulsions every 24 hours, until the total quantity reached 3 cc. for each emulsion containing 100 grams of varnish base. Drying tests were made each time right after the addition of the hydrogen peroxide and also 24 hours later. The drying tests were made on glass plates, using a Bird film applicator, depositing 0.0015 inch thick wet film.

The results show the following picture:

Ester gum varnishes

In most cases the body was of very great importance. In the case of the 50 gallon ester gum varnish 90 minutes holding time with a varnish base viscosity of B to C (in mineral spirits 50% solids) was the one which gave in less than one hour a dust-free film. 150 minutes holding time was very satisfactory. The addition of 1 cc. of hydrogen peroxide was already interesting, but a very fast drying emulsion resulted after the addition of 2 cc. of hydrogen peroxide. In the case of the 25 gallon ester gum varnish 150 minutes holding time with a viscosity D and addition of 1 cc. hydrogen peroxide was interesting and the sample batch of 180 minutes holding time, and of viscosity J was still further improved. In the case of the 12½ gallon ester gum varnish, 180 minutes holding time seemed to be needed for a fast conversion and the addition of 1½ cc. hydrogen peroxide gave improved results, with further improvement, after the addition of 2 cc. and 3 cc. respectively as total hydrogen peroxide addition.

Maleic resin varnishes

In case of the maleic type resin in 50 gallon oil length 60 minute cook, with a viscosity of B, after the addition of 2 cc. hydrogen peroxide, was interesting. The same resin of 25 gallon oil length gave improved results with 120 minutes and 150 minutes holding time, with viscosities E to F and T respectively. The 150 minutes batch gave interesting results after the addition of 1 cc. hydrogen peroxide. The same resin 12½ gallon oil length gave good results after a 30 minute cook, with a viscosity of D-E.

Modified phenolic resin varnishes

In the case of the modified phenolic resin varnishes in the 50 gallon oil length, the batch with a cooking time of 60 minutes with a viscosity I to J was satisfactory, and 1 cc. hydrogen peroxide had to be added as minimum requirement. Good results were obtained with an 85 minutes' cook and an addition of 2 cc. of hydrogen peroxide. In 25 gallon oil length a 90 minutes' cook with a viscosity of F to G and an addition of 1½ cc. of hydrogen peroxide gave good results, whereas in the 12½ gallon length the same resin yielded good results in the 60 minutes' cook with a viscosity G to H after the addition of 1 cc. of hydrogen peroxide.

The following table will show the stages of drying of the films obtained from some of the above emulsions. In all drying tests a Bird film applicator was used, deposition 0.0015" thick wet film. The tests were made on glass plates and the stages are expressed in the scale used in Example 30. The state of drying after 3 hours is only given, to express the state of the films at

a comparatively early stage, after the wet films were deposited. All these tests were carried out with the emulsions containing the full 3 cc. of hydrogen peroxide and several days after the last portion of hydrogen peroxide was added.

TABLE H

Oil Length	Resin	State of Film		Cooking Time	Viscosity Min. Sp. 50% solids
		After 1 hr.	After 3 hrs.		
50 gal.-----	Ester gum-----	K	G	120	E-F
25 gal.-----	do-----	K	H	180	J
50 gal.-----	Maleic-----	K	H	120	V
50 gal.-----	Mod. Phenolic-----	K	F	30	D
25 gal.-----	do-----	K	G	30	E
12½ gal.-----	do-----	K	A	60	G-H

In case of clear varnishes of the type described in this series, a quick film formation, that is fast demulsification causes the entrapment of large quantities of water underneath the film and may cause, for a longer period, a so-called "after tack." To overcome such difficulty it may be advisable to slow down demulsification to retard the initial film formation, so that a larger portion of the water may evaporate before the film formation would seal the surface. Certain emulsifying agents may be used, which act in a way to retard demulsification or other means known in the art may be used to achieve such purpose. If the demulsification is slowed down, the initial drying may be retarded, but the final tackfree stage is obtained at an earlier stage.

If pigments are added to the varnish emulsion, their presence usually facilitates evaporation of water and with a fast demulsification tackfree films can be obtained simultaneously with a great ease.

EXAMPLE 33.—EFFECT OF VARYING QUANTITIES OF HYDROGEN PEROXIDE ON VARNISH BASES

1,000 grams of a varnish base which was obtained by heating equal parts by weight of linseed oil containing beta-methyl anthraquinone and a maleic resin (Arochem 520) at 290° C. for one hour (yielding viscosity I when diluted with mineral spirits to 50% solids), was emulsified in the following manner:

First driers were added to the varnish base yielding 0.1% lead, 0.03% cobalt, and 0.02% manganese on the oil content. Then 100 grams of a 10% strong Duponol ME solution in water was added to the varnish base under agitation. 900 grams of water and 46 cc. of a 10% strong sodium hydroxide solution were slowly mixed into the varnish base under agitation and an emulsion was obtained having a pH of 9.1. The emulsion was divided into 3 portions. Into the first portion 1½% of hydrogen peroxide were added, whereas to the second portion 3% and to the third portion 4½% hydrogen peroxide were added, all by weight and based on the oil content. The three emulsions were tested for drying and by depositing 0.0015" thick wet films after 1 hour, the first emulsion showed stage G, the second emulsion showed stage F, and the third emulsion stage E, all in accordance with the scale referred to further above (Example 30) in this specification. These results show that the higher the peroxide content, the faster drying the emulsion becomes, under the reaction condition kept in this comparative series.

EXAMPLE 34.—VARNISH BASE WITH TERPENE RESIN

500 grams of heat bodied linseed oil (containing beta-methyl anthraquinone as heat bodying accelerator) having viscosity of Z-5 and 500 grams of polymerized terpene resin, marketed under the trade name of Piccolyte S-115 by the Pennsylvania Industrial Chemical Co., was heated to 290° C. in 65 minutes and held at that temperature for 80 minutes. Driers were added to this varnish base to yield 0.1% lead, 0.03% cobalt, and 0.02% manganese, as metal content, based on the oil present. The varnish base was emulsified by adding 10 grams of a 10% Duponol ME solution for each 100 grams of varnish base. Into that mixture, 90 gram portions of water and 1 gram portion of concentrated ammonia were added for each 100 grams of the varnish base. The emulsion so obtained had a pH of 9.7. 5% of hydrogen peroxide, 30% strong, based on the oil content was added to the emulsion and after 24 hours standing, the film deposited reached within 1 hour stage G according to the standards used in this specification.

EXAMPLE 35.—USE OF DEHYDRATED CASTOR OIL

To 400 grams of dehydrated castor oil, having a viscosity of Z-3, driers were added to yield 0.3% lead, 0.03% cobalt and 0.02% zinc, as metal, based on the oil content. Into this oil 2 grams of Emulphor ELA (a polyethyleneoxide condensation product) were mixed in, together with 1 gram of Triton K-60. Another solution was prepared of 0.5 gram of Triton NE, 1 gram of triethanolamine and 200 grams of water. Both solutions were kept at room temperature and the water solution was stirred into the oil under constant agitation gradually. The emulsion had a pH of 7.2. A 10% strong sodium hydroxide solution was added until the pH was raised to 11. 40 grams of a 30% strong hydrogen peroxide solution was added to the emulsion gradually in 20 minute intervals, during 24 hours. The emulsion yielded a solid film within 30 minutes after it was applied with a film applicator depositing 0.0015" thick wet film.

The tritons are sodium salts of various aryl-alkyl poly-ether sulphonates.

EXAMPLE 36.—PREPARATION OF GLOSSY VARNISH FILMS

It was found that increase in the viscosity of the varnish solids and a successful conversion of the emulsion to an air sensitive emulsion usually tends to cause a more or less degree of flatness of the film and that the film becomes more or less turbid, losing its transparency. The reason seems to be that in the emulsion aggregation, each dispersed particle is surrounded by a solid skin and upon demulsification this microscopic skin formation causes the flatness and turbidity, by preventing that the particles should coalesce to a uniform, transparent and homogeneous film. For many purposes, however, clear and glossy varnish films are required, and it seemed advantageous to form such films also from air sensitive emulsions. It was found that if organic solvents are present in the dispersed phase of the emulsion, they will prevent an increased degree of aggregation on the interface of oil-water, and instead will secure a uniform aggregation throughout the dispersed phase particle, so that upon demulsification solid films can be obtained, which show satisfactory gloss and transparency.

Five dispersions were prepared by using as oil ingredient M-37 linseed oil, as resin ingredient, ester gum, which has been added to the oil in the form of a 50% solid content solution in mineral spirits. In the 5 varnishes, which were dispersed, the proportion of oil to resin was varied in the following manner:

Example 36-A.—100 oil, 10 resin.

Example 36-B.—100 oil, 25 resin.

Example 36-C.—100 oil, 50 resin.

Example 36-D.—100 oil, 75 resin.

Example 36-E.—100 oil, 100 resin.

To the oil-resin mixtures, additional mineral spirits was added, to secure a total mineral spirits content amounting to one-half of the total weight of the oil plus resin mixture. The mineral spirits adjustment was made in such a way that consideration was given to the mineral spirits added by the cold cut ester gum solution, and the total mineral spirits quantity was always 50 parts on 100 parts of total varnish solids. The five mixtures were emulsified by the aid of Duponol ME, ranging in the neighborhood of 1%, based on the varnish solids. Sodium hydroxide was added to adjust the pH between 9.5 and 10. So much water was used that all emulsions had a water content around 40%. Hydrogen peroxide was added to the emulsion to the extent of 5 grams of a 30% strong hydrogen peroxide solution for each 100 grams of oil.

When testing the film qualities of the 5 emulsions here described, deposits were made of 0.0015" thick wet film on glass plates. The emulsions formed clear films between 25 and 40 minutes, yielding soft solids and all having gloss, together with clarity, as their characteristics. The two emulsions with the two highest resin content had somewhat more gloss than the others.

Instead of mineral spirits other solvents may also be used. Coal tar solvents, for instance, act to cause gloss to a greater degree than mineral spirits, however, they retard somewhat the emulsion aggregation and therefore should be used with advantage in small quantities.

EXAMPLES 37 AND 38.—THE ACTION OF OXYGEN AND OXYGEN ADSORPTION

In these two examples the action of oxygen gas is demonstrated, used as a blanket over an emulsion. In both examples a closed glass system was used, which consisted of a filter flask type glass flask, which was immersed in a constant temperature bath, maintaining the temperature of the emulsion around 60° C. The glass flask was connected with a vacuum arrangement, with a manometer registering the pressure and with a large glass container which could be filled with oxygen. The equipment used permitted a constant shaking motion of the glass flask in which the emulsion was kept. Alternative use of vacuum and an oxygen flask permitted to fill the entire volume of the equipment above the emulsion with oxygen and the volume of the equipment together with the varying pressure readable on the manometer showed the quantity of oxygen adsorbed. The necessary additional readings on the atmospheric pressure, temperature, etc., were made to eliminate experimental errors as far as possible.

EXAMPLE 37

In this example, 100 grams of M-37 oil were emulsified with 400 grams of distilled water, 10 grams Duponol ME solution, 10% strong, and

2 grams of sodium hydroxide solution, 10% strong. The original pH was 11 and the final pH was 6.6, after the treatment period. The total volume of the system was 894 cc. The emulsion had 19.5% solids. In this example after an 8 hour treatment at high temperature the shaking equipment and the heat source were shut down for a period of 60 hours and resumed after the 68th hour to complete a 90 hour experimental period. In other words, for 60 hours out of the 90 hours total time the system was at room temperature, whereas for 30 hours in total the emulsion was kept at 60° C. When plotting the figures of the quantity of the oxygen adsorbed, expressed in percents by weight, based on the oil, versus time in hours, the curve obtained shows an autocatalytic shape with an induction period running to about 68 hours, after which the oxygen quantity adsorbed was 0.34% and ended after 90 hours with a total oxygen adsorption of 3.22% by weight, based on the weight of the oil. In this particular case the long induction period was believed to be caused by the fact that for 60 hours from the first 68 hours, the emulsion was at room temperature. Therefore, Example 38 was run all the time at 60° C. It should be mentioned that after the system was opened and the emulsion tested an air sensitive emulsion resulted, having solid particles dispersed therein.

EXAMPLE 38

This was carried out very similarly to Example 37 except that somewhat less water was used, to yield 20% solids in the emulsion and 3 grams of 10% sodium hydroxide were used, to yield an original pH of 11.7. Otherwise the conditions were the same as in Example 37. In Example 38 the temperature was constantly kept at 60° C. This example was carried out in such a way that the system was broken after 65 hours. When plotting the results of oxygen adsorbed versus time, the shape of the curve was an autocatalytic one. After 18 hours about ½% oxygen was used up, whereas after 25 hours 1½% oxygen was used, and after 40 hours about 2.3% were used. After 40 hours the curve flattened out and after 65 hours the total oxygen quantity used was 2.45%, by weight, based on the oil content.

In both Examples 37 and 38 fresh quantities of oxygen were introduced into the system, as soon as such was necessary, because of the previous oxygen being used up, to the extent of at least 50%.

Also Example 38 yielded an air sensitive emulsion, having solid particles dispersed in the water phase.

It is believed that the maximum quantity of adsorbed oxygen is not needed for the emulsion aggregating process and that the adsorption phenomenon is a secondary reaction to the emulsion aggregation process. However, a critical concentration of active oxygen has to be present.

EXAMPLES 39 TO 44.—THE USE OF METALLIC DRIERS

In the standard way of emulsification six different preparations were made, having the following formulae:

EXAMPLE 39

	Grams
M-37 linseed oil.....	100
10% Duponol ME solution.....	10
Distilled water.....	400
10% strong NaOH solution.....	2

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EXAMPLE 30

M-37 oil	Grams
Naphthenate drier 6% cobalt metal content	100
10% Duponol ME solution	0.5
Distilled water	10
10% strong NaOH solution	400
	2.5

REMARK: Examples 39 and 40 are parallel experiments except that 40 had driers dispersed in the oil prior to emulsification. Larger NaOH quantity was needed in Example 40, to bring the pH near to that of Example 39.

EXAMPLE 41

M-37 linseed oil	Grams
10% Duponol ME solution	100
Distilled water	10
KH ₂ PO ₄	400
	1

EXAMPLE 42

M-37 oil	Grams
Naphthenate drier 6% cobalt metal content	100
10% Duponol ME solution	0.5
Distilled water	10
KH ₂ PO ₄	400
	1

REMARK: Examples 41 and 42 were parallel experiments. Example 42 having a metallic drier dispersed in the oil prior to emulsification.

EXAMPLE 43

M-37 linseed oil	Grams
10% Duponol ME solution	100
Distilled water	10
Hydrochloric acid, concentrated	400
	1

EXAMPLE 44

M-37 linseed oil	Grams
Naphthenate drier 6% cobalt metal content	100
10% Duponol ME solution	0.5
Distilled water	10
Concentrated hydrochloric acid	400
	1

Remark: Examples 43 and 44 were parallel experiments. Example 44 having a metallic drier dispersed in the oil prior to emulsification.

All emulsions from 39 to 44 were agitated, while kept at temperatures ranging from 60° to 65° C., the treatment being carried out for 48 hours. Sample portions of the emulsions were coagulated after 24 hours and 48 hours treatment time, using barium chloride for precipitation, and the oil products were dried at 130° C. Table I shows the results of this series.

TABLE I

Example No.	Original pH	Coagula After 24 hours, Stage	Coagula After 48 hours, Stage
39	11.0	3+I(G-CF)+	4 (NT-ST).
40	10.8	4 (NT-ST).	4+(NT-ST)+.
41	6.2	1-2 (FV) to (HV-TP)	Almost 4, Almost (NT-ST).
42	6.0	1 (FV)	3-4 (IG-CF) to (NT-ST).
43	1.8	3 (IG-CF).	4 (NT-ST).
44	1.6	1-2 (FV) to (HV-TP)	3+(IG-CF)+.

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In the above table, where two stages are given combined with "to," this means that the product was inbetween the two stages in question. The same applies when two numbers are combined by a hyphen.

Table I shows, that in the highly alkaline region the addition of drier is accelerating the emulsion aggregation, whereas in the slightly acid and in the strongly acid regions, the addition of drier retarded the conversion. This retardation in the strongly acid region was more pronounced, which may be partly due to the fact that the conversion is much more rapid in the strongly acid region, or in other words, is very slow in the slightly acid region.

Examples 39, 40, 41, and 43 yielded after 48 hours treatment air sensitive emulsions.

EXAMPLE 45.—USE OF VARIOUS EMULSIFYING AGENTS

In this example four emulsions were prepared, using the following basic formula:

M-37 linseed oil	Grams
10% strong NaOH solution	100
Distilled water	3
Emulsifying agent	500
	2

The four different preparations contained the following emulsifying agents:

Example 45-A.—Duponol ME.

Example 45-B.—Emulphor AG.

Example 45-C.—Sodium oleate flakes.

Example 45-D.—Diglycol oleate.

All preparations were kept over 3 days in covered beakers and then heated to a temperature of 60–65° C., under agitation. Precipitations were made on sample batches after 24 hours and 48 hours treatment at elevated temperatures. Table J shows the results.

TABLE J

Example No.	Original pH	Coagula After 24 hrs., Stage	Coagula After 48 hrs., Stage	pH After 48 hrs.
45-A	11.3	3-4 (IG-CF) to (NT-ST)	4+(NT-ST)+	9.2
45-B	11.7	3-4 (IG-CF) to (NT-ST)	4+(NT-ST)+	9.3
45-C	11.5	3-4 (IG-CF) to (NT-ST)	4+(NT-ST)+	9.5
45-D	11.5	Almost 4, Almost (NT-ST)	4++(NT-ST)++	9.2

These preparations shows that by using four different emulsifying agents, under otherwise comparative reaction conditions in the highly alkaline region, comparatively small differences exist. Diglycol oleate seems to accelerate to the degree of a trace the conversion, but the degree of difference was small. All the other three behaved very similarly to each other. All four were converted to air sensitive emulsions after 48 hours at elevated temperatures.

Both in Table I and in Table J the "+" sign means a more advanced stage than the one given by number or by code letters. "++" is still more advanced.

EXAMPLE 46.—AMMONIA TEST USED AS INDICATOR OF EMULSION AGGREGATION, CAUSED BY ACTIVE OXYGEN

Conversion of linseed oil to viscosity Y

This example demonstrates how readings of the ammonia test relate to the emulsion aggregation caused by active oxygen. 5,000 grams of alkali refined linseed oil was bodied in a closed stainless steel kettle under CO₂ blanket at 295° to 300° C. A portion of the batch was taken out after 5¼ hours of heating, having a viscosity of Y on the Gardner scale. The rest of the batch was further bodied for a total time of 8½ hours, yielding a viscosity between Z-5 and Z-6 on the Gardner scale.

20% solid content emulsions were prepared from both oils, using 100 grams of oil, 10 grams of a 10% Duponol ME solution, 4 grams of 10% sodium hydroxide solution, and 390 grams of distilled water. The resulting emulsion had an original pH of around 11.8. The emulsion made of the oil with Y viscosity, we shall refer to as Example 46-A and the emulsion made of the oil with Z-5—Z-6 viscosity as Example 46-B.

To Example 46-B, 5 grams of hydrogen peroxide 30% strong were added and the emulsion was kept in closed bottle, yielding after 48 hours stage 4 to 5, that is (NT-ST) to (GD), when tested with the barium chloride precipitation method.

Example 46-A was treated the same way as 46-B but it did not yield on standing at room temperature a product beyond the thermoplastic stage. Therefore, 46-A was repeated by keeping same at 60° to 65° C. under agitation, and add-

ing the first day 5 grams of 30% strong hydrogen peroxide, another 5 grams of hydrogen peroxide after 48 hours, together with 2 grams of a 10% NaOH solution, to bring the pH above 10, (after previously it dropped below this figure). The third day another 5 grams of hydrogen peroxide (30% strong) were added and after 3 days at temperatures 60° to 65° C. the emulsion was kept for 3 days at room temperature, without agitation. Then a sample batch was coagulated with barium chloride and the sample coagulum was dried at 130° C., yielding a product in stage 4 (NT-ST).

Ammonia tests were carried out with both of the oils used in preparations 46-A and 46-B. The oil used in 46-B, having a Gardner viscosity of Z-5 to Z-6 gave a positive ammonia test in less than 2 minutes, whereas the viscosity Y oil, used in 46-A was negative even after 24 hours immersion in the concentrated ammonia solution.

The above illustrates the point that where the ammonia test is positive, the emulsion aggregation caused by active oxygen may be performed by great ease, (in the case of 46-B at room temperature,) however, a negative ammonia test does not exclude the possibility of emulsion aggregation, caused by active oxygen.

Further, it may be said that in case of a linseed

oil, bodied under CO₂ blanket an oil with Y viscosity needs simultaneous use of several factors which we know accelerate emulsion aggregation, such as low solid content, increased temperatures, the use of hydrogen peroxide, and agitation. Obviously, a linseed oil product, containing activating agents or another oil containing conjugated double bonds may be transformed under the conditions of Example 46-A even with a somewhat lower viscosity than viscosity Y, such as viscosity Q. Both 46-A and 46-B were air sensitive emulsions after completion of the herein described treatments.

EXAMPLE 47.—THE USE OF VARIOUS ALKALI HYDROXIDES

In this example a 20% solid content M-37 oil emulsion was prepared, using methods described further above and using on 100 grams oil, 10 grams of a 10% Duponol ME solution and 390 grams of distilled water. Several thousand grams of this emulsion were prepared.

The pH of three different samples was brought to about 11, using ammonium hydroxide in one case, sodium hydroxide in another case, and potassium hydroxide in the third case. On a 500 gram batch of this emulsion, 10 grams of concentrated ammonium hydroxide, 2 grams of a 10% strong NaOH solution and 2 grams of a 10% strong KOH solution were needed respectively, to yield pH 11. 5 grams of hydrogen peroxide, 30% strong were added to each of the 3 emulsions and they were kept at room temperature, without agitation for several days. Sample batches were coagulated after 24 hours and after 72 hours, giving the results recorded in Table K.

TABLE K

Alkali Used	Initial pH	After 24 hrs.		After 72 hrs., Stage
		Stage	pH	
Ammonium Hydroxide.....	11	3-4 (IG-CF) to (NT-ST).	9.5	4-5 (NT-ST) to (GD).
Sodium Hydroxide.....	10.8	3 (IG-CF).....	8.3	4-5 (NT-ST) to (GD).
Potassium Hydroxide.....	10.7	3 (IG-CF).....	8.5	4-5 (NT-ST) to (GD).

This example shows that different sources responsible for the pH do not change the reaction to any considerable extent. The product with ammonium hydroxide accelerated the conversion to a very slight degree in the early stages and yielded a lighter colored coagulum. All three preparations were air sensitive emulsions after 72 hours of storage.

EXAMPLE 48.—CONVERSION IN PRESENCE OR ABSENCE OF PIGMENTS

The comparative preparations of this example are designed to show that conversion, that is emulsion aggregation by the aid of active oxygen may occur also in presence of pigments.

Example 48-A.—400 grams of M-37 oil were mixed with naphthenate driers, yielding 0.1% lead, 0.03% cobalt and 0.05% zinc as metal, based on the oil content. The driers, the oil and 100 grams of titanium dioxide pigment were milled and homogenized on a laboratory 3-roller mill. 100 grams of this mixture, 10 grams of 10% Duponol ME solution and 1 gram of oleic acid were mixed, while the mixture was slightly warmed up, to secure mobility. This mixture was emulsified by 90 grams of water and 3 grams of a 25% strong sodium hydroxide solution, by adding the latter mixture to the oil mixture slowly, under stirring. The resulting emulsion had a

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pH of 10.9. 4 grams of 30% strong hydrogen peroxide were slowly added to the emulsion during the course of 15 minutes.

Example 48-B.—A similar emulsion than 48-A was prepared in absence of pigments, using 100 grams of M-37 oil, 1 cc. oleic acid, the same naphthenate driers as used in 48-A, 10 grams of 10% Duponol ME solution, 90 grams of distilled water, 3 grams of 25% sodium hydroxide, yielding an oil-in-water emulsion of a similar pH as 48-A. 5 grams of hydrogen peroxide were added, to keep the proportion similar to the same used in 48-A.

Example 48-C.—48-A was repeated, using zinc oxide instead of titanium dioxide. Otherwise, the preparation was made the same way as 48-A.

After 24 hours storage, films were prepared from 48-A, 48-B and 48-C, depositing 0.0015" wet film. In all three cases, demulsification occurred in about 30 minutes and the films were soft solids right after demulsification. 48-A and 48-C seemed to be somewhat tougher and harder, than 48-B. Therefore, it may be concluded that emulsion aggregation may be carried out in presence of pigments, which have been predispersed in the oil, prior to emulsification, and further that in presence of pigments the films seem to be harder, possibly because of the physical presence of the pigments in the film.

All three preparations of this example are air sensitive emulsion type coating materials.

EXAMPLE 49.—GLOSSY FILM WITH TOLUOL

100 grams of M-37 linseed oil and 100 grams of ester gum were heated together to 150° C., to obtain a clear melt and blend. The mixture was cooled slightly and 40 grams of toluol were added at a temperature preventing extensive evaporation of the solvent. Naphthenate driers were added, to yield 0.1% lead, 0.03% cobalt and 0.05% zinc, as metal, based on the oil content. 24 grams of a 10% Duponol ME solution were mixed into the mixture. Another mixture was prepared by mixing 150 grams of distilled water and 4.5 grams of a 10% Duponol ME solution. The aqueous mixture was slowly added to the varnish base mixture, under agitation. An emulsion was obtained, having pH 9.9. 5 grams of a 30% hydrogen peroxide were mixed into the emulsion and the preparation was stored for 48 hours. 0.0015" wet film was deposited from this emulsion, forming a clear film in about 30 minutes. Right after demulsification the film obtained was solid, had a high gloss, but had a slight surface tack.

In most cases, when air sensitive emulsions are made according to processes described in the examples further above, more or less flat surfaces are obtained. This is believed to be caused by the fact that a solid skin is formed around the particles, during the aggregation process, which has an increased degree of solidity, when compared with the interior portion of the dispersed phase particle. Upon demulsification this solid skin prevents that the particles should coalesce to a transparent uniform film. It is also possible that the flatness is caused by turbidity, which in turn is caused by trapped water particles. It is of great importance to deposit glossy films from emulsions and this aim is difficult to achieve with most emulsions. It is increasingly difficult to achieve with air sensitive emulsions. It was thought that the presence of a small quantity of an organic solvent will prevent skin formation as an envelope of the dispersed phase particle and will also cause complete demulsification, ex-

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cluding trapped water particles from the film. Example 49 shows the success obtained with the application of a small quantity of an organic solvent.

On the score of gloss it should be mentioned that the higher the oil is bodied prior to emulsification, the more it tends to form flat films. Further, in case of oil-varnish-resin mixtures, the higher the resin proportion, the clearer the films become.

The product of Example 49 is an air sensitive emulsion, useful as coating material and e. g., it may be used in the formula of Example 30, in making a flat wall paint, replacing the emulsion used in that example.

EXAMPLE 50.—VARYING DEMULSIFICATION TIME

Three dispersions were prepared in the following manner:

Example 50-A.—100 grams of M-37 linseed oil, 25 grams of ester gum, 10 grams of toluol, naphthenate driers yielding 0.1% lead, 0.03% cobalt, and 0.05% zinc, as metal content, based on the oil, 2 cc. of linseed oil fatty acids were mixed (resin was molten first in the oil), and emulsified with 125 grams of water, containing 5 grams of concentrated ammonium hydroxide. The resulting emulsion was treated with 5 grams of hydrogen peroxide (30%).

Example 50-B.—A similar preparation, than 50-A was prepared, with the only difference that in this preparation 5 cc. of linseed oil fatty acids and 10 grams of concentrated ammonium hydroxide were used.

Example 50-C.—Example 50-A was repeated, however, increasing the linseed oil fatty acid quantity to 10 cc., and the ammonium hydroxide quantity to 15 grams.

0.0015" thick wet films were deposited from the above 3 dispersions and the demulsification time was noted, yielding the following results:

Example Number	Demulsification Time
	Minutes
50-A.....	31
50-B.....	41
50-C.....	105

These results show that increasing soap quantities in an air sensitive emulsion increase the demulsification time. Differences in pH values are not believed to be connected with demulsification velocity.

As a measure of demulsification in this example and elsewhere in this specification, we took the time required for complete disappearance of milkiness from the deposited film. In other words, disappearance of the last traces of milkiness was considered as end-point of demulsification. Milkiness indicates existence of an emulsion.

GENERAL REMARKS

(a) In my Patent 2,007,958, I prepared rubber-like masses, out of bodied oils, which contained a metallic soap before emulsification. Such metallic soaps either were incorporated into the oils to form solidified oils, by direct addition, or the metallic soaps were formed in situ from salts, during heat bodying of the oil. Examples of the latter alternative are carbonates, sulphides and sulphites, which form soaps with the fatty oils at heat bodying temperatures, while evolving CO₂, or H₂S, or SO₂ gas.

I found that where a soap (e. g. a metallic soap) is incorporated in a heat bodied oil and such an oil is used in preparing coating materials, the films obtained have reduced water resistance, apparently because the soaps remaining in the films cause a constant swelling or even re-emulsification of the film. Therefore, in my present process I use with preference soap-free fatty oils and obtained thereby satisfactory weathering qualities of the films deposited from my coating composition.

(b) The Gardner scale, used in this specification is described in detail on page 217 of the 9th edition (1939) of "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," by Henry A. Gardner, published by the Institute of Paint and Varnish Research, 1500 Rhode Island Avenue, N.W., Washington, D. C.

(c) It should be mentioned, summarizing some aspects of this invention, that in case no oxygen addition is used to bring about the emulsion aggregation, in addition to the oxygen adsorbed in the water, the products so obtained are much more durable, as they are free of splitting-off products, caused by oxidation and also free of oxidation products of the ester molecule. Oxidation products in general are undesirable in coating materials, as they reduce water resistance and the life of the film.

It is of advantage if the oxygen content of the esters of my invention does not increase during the emulsion aggregation process to an extent larger than ½%, when compared to the oxygen content of the ester prior to emulsification.

(d) Flat wall paints made according to my process should preferably have a pigment volume ratio of 35% or more.

(e) The esters used in my emulsion aggregation process are always thermoplastic before emulsification, which means that they are either in a fluid state at room temperature or can be reversibly fused to form a liquid.

(f) The organic solvents I may use in my process are of the type, which are immiscible with water and which dissolve the esters and/or resins present in the dispersed phase of my emulsions.

(g) When working my process on the alkaline side, I found that 8.4 is the pH limit, which has to be reached for the purpose that the emulsion aggregation should proceed with a reasonable and practical speed. However, to enable me to obtain the effect with the addition of as small a quantity of per-compound as possible when working at room temperature, I need pH 10 as lower limit and preferably 10.5. By working at such high pH values, the per-compound needed is so small, that the oxidation process is reduced to a reasonable and desirable low proportion. This is advantageous, as explained above, to avoid the formation of secondary reaction products, which are undesirable in coating materials.

I found further that I have rarely cause to increase the pH above 13.

I claim:

1. The process in preparing oil-in-water air sensitive emulsions of soap-free fatty oils having drying characteristics, which yield solid and coherent films upon demulsification, comprising the steps of (1) bodying the fatty oil to a viscosity within the range of 15 to 800 poises, (2) emulsifying said bodied fatty oil in water to form an oil-in-water emulsion, (3) bringing the pH of the emulsion to at least 8.4, and (4) exposing the dispersed phase of the emulsion to the action of

active oxygen, until the dispersed phase particles solidify in the emulsion.

2. The process in preparing oil-in-water air sensitive emulsions of soap-free bodied esters of a polyhydric alcohol formed with acids of fatty oils, said esters having drying characteristics and having in a fatty acid part of the molecule more than one double bond, said emulsion being useful in coating materials, comprising the steps of (a) bodying the ester at least to a degree such that when heated at 160° C. with 4½% sulfur an irreversible gel will form within a period not exceeding 4 hours, but not beyond a degree to have a body heavier than that which would result in conversion to an irreversible gel in less than 15 minutes when vulcanized with ½% sulfur at 120° C., (b) emulsifying said bodied ester in water to form an oil-in-water emulsion, (c) bringing the pH of the emulsion to at least 8.4, but not above 13, and (d) exposing the dispersed phase of the emulsion to the action of active oxygen, until the emulsified bodied ester particles solidify in the emulsion.

3. The process of claim 2, in which the dispersed phase of the emulsion comprises a blend of a fatty oil and of a varnish resin.

4. The process of claim 2, in which a compound supplies the active oxygen, which is capable to release oxygen in situ in the presence of water.

5. The process of claim 2, in which a peroxide supplies the active oxygen.

6. The process of claim 2, in which an oxygen containing gas current supplies the active oxygen.

7. The process of claim 2, in which the bodied ester content of the emulsion does not exceed 33%.

8. The process of claim 2, in which the bodied ester content of the emulsion does not exceed 20% of the combined weight of varnish solids and water.

9. The process of claim 2, in which during step (d) the temperatures range between 50° C. and the boiling point of the emulsion.

10. The process of claim 2, in which during step (d) the emulsion is mechanically agitated.

11. The process of claim 2, in which step (d) is carried out under reduced pressure.

12. The process of claim 2, in which the bodied ester is a bodied linseed oil.

13. The process of claim 2, in which the bodied ester is a bodied fatty oil, having a conjugated double bond in a fatty acid constituent.

14. The process of claim 2, in which the bodied ester is an alkyd resin, said alkyd resin containing in its acid constituent at least 50% of fatty acids.

15. The process in preparing oil-in-water air sensitive emulsions of soap-free fatty oils having drying characteristics, which yield solid and coherent films upon demulsification, comprising the steps of (1) bodying the fatty oil to a viscosity within the range of 15 to 800 poises, (2) emulsifying said bodied fatty oil in water to form an oil-in-water emulsion, (3) bringing the pH of the emulsion to at least 10 but not exceeding 13, and (4) exposing the dispersed phase of the emulsion to the action of active oxygen, until the dispersed phase particles solidify in the emulsion.

16. The process of claim 2 in which the polyhydric alcohol component of the bodied ester is at least tri-hydric.

17. The process of claim 2, in which the dispersed phase of the emulsion comprises a blend of a fatty oil and of rosin.

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18. The process of claim 2 in which the dispersed phase of the emulsion contains an organic solvent as a minor constituent, said solvent being water immiscible.

19. The process in preparing oil-in-water air sensitive emulsions of soap-free bodied esters of a polyhydric alcohol formed with acids of fatty oils, said esters having drying characteristics and having in a fatty acid part of the molecule more than one double bond, said emulsion being useful in coating materials, comprising the steps of (a) bodying the ester at least to a degree such that when heated at 160° C. with 4½% sulfur an irreversible gel will form within a period not exceeding 4 hours, but not beyond a degree to have a body heavier than that which would result in conversion to an irreversible gel in less than 15 minutes when vulcanized with ½% sulfur at 120° C., (b) emulsifying said bodied ester in water to form an oil-in-water emulsion, (c) bringing the pH of the emulsion to at least 10.5, but not above

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13, and (d) exposing the dispersed phase of the emulsion by the action of active oxygen, until the emulsified bodied ester particles solidify in the emulsion.

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