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MAKING COATING MATERIAL EMULSIONS

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1

In my British Patents 318,562, 321,892, and 341,490 as well as in my United States Patent 2,007,958, I have produced plastic masses out of fatty oils by the 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 as "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 in between 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, by employing the

2

oxygen content adsorbed in the water phase of the emulsion, as more fully described here below. Advantageously the pH value of the emulsion is retained 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 perform 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
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.

For the purposes of this specification under fatty acid esters I understand 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 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.

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:

Rosin,
Esters of rosin with polyhydric alcohols, (glycerine, glycols, pentaerythritol, sorbitol, mannitol, etc.)
Congo,
Congo esters,
Other Copals (e. g. Kauri),
Cumar and Indene resins,
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 suitably 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 SO_2, H_2S, CO_2, N_2, etc., either to blanket the oils 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:

In the first place, the oil should be boiled 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.

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.

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 lengths 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. 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 ofter 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 to 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.

In my copending application Serial No. 521,441, filed February 7, 1944, dealing with a somewhat related subject matter, I have described several means how to obtain my active oxygen. In my present process I am using such oxygen solely, which is present in the water phase of the emulsion, in form of adsorbed oxygen, or which may be adsorbed freely by the water phase from the atmosphere blanketing the emulsion, during the aggregation process.

As the oxygen, which is adsorbed in the water phase, acts regularly in a slow manner, it is important to use means and ways to activate this adsorbed oxygen, so that the active oxygen so formed may produce the effect desired for my emulsion aggregation process.

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 adsorbed 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 adsorbed in water and agitation causes also an increase in the movement of adsorbed gas particles. The combination of agitation and heat causes increased and combined activation.

In my present process, where only the oxygen present by natural adsorption 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.

Another way to activate the adsorbed oxygen is by treating the emulsion with energy being in the form of radiating energy of various wave lengths, such as ultra-violet light, X-rays, etc., which are known to ionize air.

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 1.)

In my present process, in which oxygen is not introduced by artificial means into the emulsion, the products 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.

Critical Hydrogen Ion 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. When working on the alkaline side, I found that it is rarely necessary to work at a pH higher than 13.

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 alkaline 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 adsorbed oxygen only, as aggregating agent, with comparatively low temperatures and slow agitation. However, using higher concentrations it may become necessary to use strongly activating conditions, such as the simultaneous use of heat, agitation, ultra-violet light radiation and/or vacuum.

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 compaartively 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.

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
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.	Polyethyleneoxide condensation product.
Nekal A, General Dyestuff Corporation.	Sodium salt of alkyl-substituted naphthalene sulphonate.
Igepon, General Dyestuff Corporation.	Sodium sulphonate of an oleic acid ester of an aliphatic compound, for instance, of the type of $C_{17}H_{33}CON—CH_3C_2H_4SO_3Na$.
Triton, Rohm & Haas	Sodium salt of aryl alkyl poly ether sulphonate.
Darvan #1, R. T. Vanderbilt Company.	Polymerized sodium salts of alkyl naphthalene sulphonic acids.
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 found that from the various emulsifying agents such types are most suitable, which are also active on the acid side, while being active on the alkaline side, too. The non-ionic emulsifying agents are belonging to that class, for instance, Pentamul 126 and 147, nonaethyleneglycolmonooleate, or the corresponding dioleate, or the corresponding monolaurate or dilaurate. (Glyco products.) A further satisfactory group is the one of the cation-active emulsifying agents. Examples are the quaternary ammonium salts. As it will be seen, the fatty alcohol sulphates (for instance, Duponol ME) are also suitable for my process.

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 thermoplastic.
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, 3, 4, 5, 6, 7–B, 7–C, 8–A, 9, 12, 13, 14 to 19, and 20 belong to this group, and also to a certain extent Example 21. 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 10, 11 and 21 describe the preparation of finished materials, such as coating compositions. Example 10 describes a bristle setting compound, Example 11 an adhesive composition and Example 21 with its various embodiments, varnish emulsions of different kinds.

EXAMPLE 1.—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 1–A) was placed in a glass tube in such a way that ⅓ of the tube

was filled with the emulsion and ⅔ 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 1–B) was kept as a control in a beaker covered by a watch glass and therefore being in constant contact 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 2 TO 9

EXAMPLE 2.—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 obtained 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 3 TO 5.—VARIATION OF PH

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 3

To 3,000 grams of the master batch emulsion of Example 2, 43 grams of $Na_2HPO_4.12H_2O$ was added as buffer. To vary the pH, the following preparations were made:

Example 3–A.—500 grams emulsion of Example 3, without additions, pH 8.4.

Example 3–B.—500 grams emulsion of Example 3, plus 10 grams of a 1% NaOH solution, pH 9.4.

Example 3–C.—500 grams emulsion of Example 3, plus 20 grams of 1% NaOH solution, pH 10.4.

Example 3–D.—500 grams emulsion of Example 3, plus 30 grams of a 1% NaOH solution, pH 10.8.

Example 3–E.—500 grams emulsion of Example 3, 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 4

3,000 grams of the master batch emulsion of Example 2 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 4–A.—500 grams of the emulsion of Example 4, unchanged, pH 2.8.

Example 4–B.—500 grams of emulsion of Example 4, plus 0.8 grams NaOH, pH 4.8.

Example 4–C.—500 grams of emulsion of Example 4, plus 1.0 gram NaOH, pH 5.7.

EXAMPLE 5

A similar emulsion to the one of Example 2 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 $Na_2HPO_4.12H_2O$, 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 wasy almost 4 on our scale (NT–ST), and was in between stage 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 6

500 grams of master batch emulsion of Example 2, was used in this example and the pH was adjusted by the addition of NaOH to be 12.2. The

emulsion was heated to 60° C. and kept there for 14 hours, under agitation. Samples were taken out after 6 hours and 14 hours. The pH of the emulsion dropped to 10.5, after the heat treatment and a further 10 hour storage period. A portion of the sample batches was coagulated with barium chloride and dried. After 6 hours treatment the coagulum was in the state of (HV–TP), being thermoplastic. After 14 hours the coagulum was almost in the state of (NT–ST), showing a good progress of the emulsion aggregation process. After a further 8 hour treatment, the coagulum reached the stage of (NT–ST).

EXAMPLE 7.—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 7–A.—At room temperature of 23° C.
Example 7–B.—At a temperature of 38° C.
Example 7–C.—At a temperature of 50° C.

Samples were coagulated after 48 hours, 72 hours and 120 hours.

The results were as follows:

TABLE A

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

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

EXAMPLE 8.—VARYING pH VALUES

Three portions of the master batch emulsion of Example 2 were used in this comparative series. Various pH values were established in the three portions, as follows:

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

8–B.—Acidified with sodium acid phthalate and pH adjusted to 5.7.

8–C.—This batch was rendered approximately neutral with mono-sodium phosphate.

These three preparations were kept at 60° C. for 96 hours, replacing the water, which evaporated. Sample quantities of each emulsion were coagulated after 16 hours, 40 hours, and 96 hours in each of the three individual cases. The following table summarizes the readings:

TABLE B

Example	pH	After 16 hr. treatment	After 40 hr. treatment	After 96 hr. treatment
8-A	2.8	(IG-CF) to (NT-ST)	(NT-ST)	(NT-ST) to (GD).
8-B	5.7	(FV)	(HV-TP)	Almost (NT-ST).
8-C	7.2	(FV)	(FV)	(IG-CF) to (NT-ST).

The three examples of this comparative series show that the transformation is very slow near the neutrality point. When working on the acid side the transformation is slow in the neighborhood of pH 5.7 and much faster at pH 2.8.

EXAMPLE 9.—EFFECT OF CLOSED FULL CONTAINERS VS. AGITATION

In this example an emulsion of the type described in Example 2 was used, adjusting the pH to 11.5, having a solid content of 20%. The emulsion was divided into 3 portions. 9–A was stirred constantly in an open beaker at a temperature of 65° C. 9–B was filled in a bottle, filling up the bottle completely and closing same with an air-tight stopper. The bottle was kept at room temperature. 9–C.—This was a repeat of 9–B, but the bottle was kept in a thermostat at a temperature of 63° C. After 48 hours, sample portions of all three preparations were coagulated with barium chloride and dried. 9–A, which was in an open beaker and was agitated, was in a stage of (NT–ST) after 48 hours. 9–B and 9–C, after 48 hours, were both still thermoplastic and viscous oils, however 9–C was in a more advanced stage, than 9–B. This shows that if only the oxygen adsorbed by the water phase is used for the emulsion aggregation process as a source of the active oxygen, access to further oxygen entry, application of heat and agitation are desirable for a fast conversion, even if the solids are comparatively kept low and the pH is in an active range. In closed containers application of heat alone is also showing some accelerating effect.

EXAMPLE 10.—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.

I. Preparation of oil emulsion

100 grams of linseed oil bodied at 300° C. under vacuum while bubbling SO_2 gas through the oil, (at the rate of 20 grams per hour for an 8,000 gram batch, in a 22 liter flask, at a vacuum of 100 mm. Hg pressure), 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 sulfur paste

32 grams of sulfur, 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 11.—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 gram 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 12 AND 13.—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 12

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, where as 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 13 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 13

This was carried out very similarly to Example 12 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 12. In Example 13 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 12 and 13 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 13 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 aggregation 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 14 TO 19.—THE USE OF METALLIC DRIERS

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

EXAMPLE 14

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

EXAMPLE 15

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

REMARK: Examples 14 and 15 are parallel experiments except that 15 had driers dispersed in the oil prior to emulsification. Larger NaOH quantity was needed in Example 15, to bring the pH near to that of Example 14.

EXAMPLE 16

	Grams
M–37 linseed oil	100
10% Duponol ME solution	10
Distilled water	400
KH_2PO_4	1

EXAMPLE 17

	Grams
M–37 oil	100
Napthenate drier 6% cobalt metal content	0.5
10% Duponol ME solution	10
Distilled water	400
KH_2PO_4	1

REMARK: Examples 16 and 17 were parallel experiments. Example 17 having a metallic drier dispersed in the oil prior to emulsification.

EXAMPLE 18

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

EXAMPLE 19

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

REMARK: Examples 18 and 19 were parallel experiments. Example 19 having a metallic drier dispersed in the oil prior to emulsification.

All emulsions from 14 to 19 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 C shows the results of this series.

TABLE C

Example No.	Original pH	Coagula After 24 hours, Stage	Coagula After 48 hours, Stage
14	11.0	3+(IG-CF)+	4 (NT-ST).
15	10.8	4 (NT-ST)	4+(NT-ST)+.
16	6.2	1-2 (FV) to (HV-TP)	Almost 4, Almost (NT-ST).
17	6.0	1 (FV)	3-4 (IG-CF) to (NT-ST).
18	1.8	3 (IG-CF)	4 (NT-ST).
19	1.6	1-2 (FV) to (HV-TP)	3+(IG-CF)+.

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 C 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 14, 15, 16, and 18 yielded after 48 hours treatment air sensitive emulsions.

EXAMPLE 20.—USE OF VARIOUS EMULSIFYING AGENTS

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

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

The four different preparations contained the following emulsifying agents:

Example 20–A.—Duponol ME.
Example 20–B.—Emulphor AG.
Example 20–C.—Sodium oleate flakes.
Example 20–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 D shows the results.

TABLE D

Example Number	Original pH	Coagula After 24 hrs., Stage	Coagula After 48 hrs., Stage	pH After 48 hrs.
20-A	11.3	3-4 (IG-CF) to (NT-ST)	4+ (NT-ST)+	9.2
20-B	11.7	3-4 (IG-CF) to (NT-ST)	4+ (NT-ST)+	9.3
20-C	11.5	3-4 (IG-CF) to (NT-ST)	4+(NT-ST)+	9.5
20-D	11.5	Almost 4, Almost (NT-ST)	4++(NT-ST)++	9.2

These preparations show that by using four different emulsifying agents, under otherwise comparative reaction conditions in the highly alkaline region, comparatively small differences exist. Diglycol oleate (diethylene-glycol 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 C and in Table D the "+" sign means a more advanced stage than the one given by number or by code letters. "++" is still more advanced.

EXAMPLE 21.—COMPARATIVE SERIES OF VARNISH BASES, WITH VARIOUS RESINS, VARYING VISCOSITIES, AND COOKING TIMES

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 [1]	Ammonia Test
90	E	Negative.
120	I	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).

The results show the following picture:

Ester gum varnishes

These varnishes were cooked at 290° C. The following list shows the time of cook necessary, to obtain at the given pH after 96 hours storage period at room temperature, a film, which is in the dust-free stage in not more than 1 hour, when applied to yield a wet-film thickness of 0.0015''. After the individual cooking time there are given in brackets the Gardner viscosities of the oleo-resinous varnish base, when thinned to 50% solids with mineral spirits, at the cooking time designated.

50 gallon lengths 120'---------- (E–F)
25 gallon lengths 150'---------- (D)
12½ gallon lengths 19'---------- (A)

Maleic resin varnishes

These varnishes were cooked at 260° C. The following are the results corresponding to the ones given for ester gum varnishes.

50 gallons 120'---------- (R)
25 gallons 120'---------- (E–F)
12½ gallons 60'---------- (E)

Modified phenolic resin varnishes

These varnishes were cooked at 290° C. The following are the results corresponding to the ones given for ester gum varnishes.

50 gallons 85'---------- (N–O)
25 gallons 60'---------- (G–H)
12½ gallons 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.

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 CO_2, or H_2S, or SO_2 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 because 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 a reasonable speed, I need pH 10 as lower limit and preferably 10.5. By working at such high pH values, the oxidation process, if any, 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.

(*h*) The air sensitive emulsions of the present process may be mixed with other emulsions, to form coating materials. Also pigments may be added to them by grinding or by other known means, to form emulsion paints or emulsion enamels. It is also possible to disperse the pigments in the oil containing emulsion solids, prior to emulsification.

(*i*) With regard to the question of activating the adsorbed oxygen, I wish to recapitulate that

application of heat, agitation, the application of vacuum, and the treatment with oscillating energy, further the use of low solid content emulsions, are the factors, which seem to achieve this desired effect.

As it is pointed out further above in this specification, the following steps activate the adsorbed oxygen present in the water phase of the emulsions of this process:

I. Agitation of the emulsion,

II. Application of heat to the emulsion, elevating its temperature above room temperature, but not above the boiling point of the emulsion (50° C. to 80° C. being good ranges of such elevated temperatures).

III. Treating the emulsions with energy being in the form of radiating energy of varying wave lengths, which are known to ionize air, and

IV. Applying vacuum to the reaction chamber in which the emulsion is kept, by reducing the pressure of the gaseous atmosphere above the emulsion to below atmospheric pressure.

These steps may be applied individually or in combination with each other.

I claim:

1. The process in preparing oil-in-water type air sensitive emulsions of fatty oils, which yield solid and coherent films upon demulsification, consisting of the steps of (1) bodying the fatty oil to a viscosity of at least Q on the Gardner scale, said bodied fatty oil showing flow characteristics at room temperature, (2) emulsifying said bodied fatty oil in water by the aid of an emulsifying agent which is stable under the reaction conditions of the process, (3) bringing the pH to lie outside of the range of 5.7 to 8.4, (4) activating the adsorbed oxygen, present in the water phase of the emulsion and (5) exposing the dispersed phase of the emulsion to the action of the activated adsorbed oxygen for at least six hours and until the viscosity of said dispersed phase is substantially increased.

2. The process of claim 1, in which the pH of the emulsion during steps (4) and (5) of the process is between 10 and 13.

3. The process of claim 1, in which the pH of the emulsion during steps (4) and (5) of the process is at least 10.5.

4. The process of claim 1, in which the pH of the emulsion during steps (4) and (5) of the process does not exceed 2.8.

5. The process of claim 1, in which the fatty oil is bodied to at least Y on the Gardner scale, prior to emulsification.

6. The process in preparing oil-in-water type air sensitive emulsions of soap-free bodied esters of a polyhydric alcohol formed with acids of fatty oils, said esters having in a fatty acid part of the molecule more than one double bond, said emulsion being useful in coating materials, consisting of the steps of (*a*) bodying the ester at least to a degree such that when heated to 160° C. with 4½% sulfur an irreversible gel will form within about 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 by the aid of an emulsifying agent which is stable

under the reaction conditions of the process, (*c*) bringing the pH of the emulsion to lie outside of the range of 5.7 to 8.4, (*d*) activating the adsorbed oxygen, present in the water phase of the emulsion, and (*e*) exposing the dispersed phase of the emulsion to the action of the activated adsorbed oxygen for at least six hours and until the viscosity of said dispersed phase is substantially increased.

7. The process of claim 6, in which the dispersed phase of the emulsion comprises a varnish resin, in addition to an ester of the fatty oil type.

8. The process of claim 6, in which the bodied ester content of the emulsion does not exceed 50%.

9. The process of claim 6, in which the bodied ester content of the emulsion does not exceed 20% of the combined weight of varnish solids and water.

10. The process of claim 6, in which steps (*d*) and (*e*) of the process are carried out at temperatures ranging from 50° C. and the boiling point of the emulsion.

11. The process of claim 6, in which steps (*d*) and (*e*) of the process are carried out while the emulsion is mechanically agitated.

12. The process of claim 6, in which steps (*d*) and (*e*) of the process are carried out under reduced pressure.

13. The process of claim 6, in which the bodied ester is a heat bodied fatty oil, having drying characteristics.

14. The process of claim 6, in which the bodied ester is a bodied linseed oil.

15. The process of claim 6, in which the bodied ester is a bodied fatty oil, having a conjugated double bond in a fatty acid constituent.

16. The process of claim 6, in which the bodied ester is an alkyd resin, comprising in its acid component at least 50% of drying and semi-drying fatty acids.

17. The process of claim 6, in which steps (*d*) and (*e*) of the process are carried out in a closed vessel, the pressure in which is below that of atmospheric pressure.

18. The process of claim 6, in which, while steps (*d*) and (*e*) of the process are carried out, the emulsion is treated with X-rays.

19. The process of claim 6, in which, while steps (*d*) and (*e*) of the process are carried out, the emulsion is treated with ultra-violet rays.

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