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PRODUCTION OF WATER DISPERSIONS OF
DRYING OILS, VARNISHES, AND LAC-
QUERS

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The invention relates to a process for the production and manufacture of emulsions of oxidized drying oils, and of varnishes, lacquers and like coating compositions containing such oils.

Processes for the production and manufacture of such emulsions are known. Processes are known to prepare oxidation products of drying oils by emulsifying the oils in water and by passing air or oxygen through this emulsion. Moreover, processes are known for the production and manufacture of emulsions of oxidized drying oils, and of varnishes and lacquers containing such oils, to which emulsions alkaline substances are added during or before the emulsions are oxidized, the emulsions thus being kept alkaline during and after oxidation. In these known processes the quantity of alkaline substances added to the emulsion will keep the pH at least as high as 7. The use of dispersions of this type is limited. The presence of large quantities of stabilizing agents and water soluble salts impairs the water resistance and the presence of even small quantities of alkaline substances causes saponification during the evaporation of the water from the dispersion after the coating composition has been applied.

The present invention is based on the discovery that stable dispersions containing oxidized oils can be produced by oxidizing such dispersions in the presence of certain dispersing, emulsifying and stabilizing agents which are stable both in acidic and alkaline media and which do not require the addition of agents for neutralizing the acids which are formed as by-products during the oxidation of the oil or oils in the dispersion.

One class of agents suitable for the above purpose comprises non-ionic dispersing, emulsifying and stabilizing agents, such as esters of long chain fatty acids, for example, nonaethyleneglycolmonooleate, higher fatty alcohols, for example, dodecylalcohol, and also polyethyleneoxide condensation products. Addition of agents of this class enables oxidation of the dispersions without impairing stability either in acidic or in alkali media. Moreover, such dispersions do not require special addition agents for neutralizing the acids formed during oxidation. However, the charge of the dispersed particles will be positive in acidic medium only, while in alkaline medium the charge is negative.

Instead of using non-ionic substances, so called cationic active long chain organic compounds may be used as dispersing, emulsifying and stabilizing agents, such as cationic and in-

vert soaps and similar products. A product of this type consists of a hydrocarbon chain which is attached to a positive group such as a quaternary ammonium group, or a sulfonium, pyridinium or phosphonium group which, together with the long hydrocarbon chain, form a positive ion when dissolved or dispersed in water. Specific examples of such products are: Cetylpyridinium-bromide, dodecyltrimethylammonium-bromide and stearyltrimethylammonium-bromide. When using cation active electrolytes as emulsifying agents in large enough quantity, positively charged dispersions can be obtained which will not reverse the charge either in alkaline or in acidic medium.

Dispersing, emulsifying and stabilizing agents of the above nature can be added to the dispersion either before, during or after emulsification, and either before or during the oxidation process. It is only important that the process of oxidation be carried out and completed in the presence of dispersing, emulsifying and stabilizing agents other than anionic.

In carrying out the process of the present invention it is often of advantage to use agents which are combinations of non-ionic and cation active substances of the above nature. Such combinations have the advantage that more stable dispersions can be obtained and smaller amounts of emulsifying agents are required. When both nonionic and cation active substances are used, the charge will depend on the pH of the emulsion and on the ratio of such product present.

By making dispersions in the above described manner and oxidizing the same, stable oxidized dispersions can be obtained without the addition of neutralizing agents and buffering substances.

It is apparent from the above considerations that the main feature of this invention consists in the oxidation of the dispersions in the presence of dispersing, emulsifying and stabilizing agents which are not active as anions and which will yield stable emulsions in acidic medium also.

Acidic dispersions containing oxidized oils, as obtained by the process of this invention are a great improvement in the technical art since the by-products of decomposition from the oxidation of the drying oils are volatile, and the deposits or films obtained from such dispersions will be free of impurities after evaporation of the water, whereas in the presence of alkaline substances the acidic decomposition products from salts which are non-volatile. Considering these facts

it will readily be understood that the water resistance of the products obtained from acidic dispersions will be much superior to those obtained by the use of alkaline dispersions. Furthermore, dispersions made according to this invention can be either positively or negatively charged, and the dispersed particles can be deposited on surfaces carrying opposite charge, or if desired such deposition can be prevented by adjusting the sign of the charge to be the same. Moreover, the amounts of emulsifying, stabilizing and dispersing agents necessary to produce a stable oxidized dispersion will be much less than with known methods.

The presence of small quantities of anionic dispersing agents does not affect the above outlined properties of the dispersions; neither does the presence of solvents for the drying oils.

Example 1.—To 100 parts of blown linseed oil the usual dryers such as 0.5% lead, 0.03% cobalt and 0.02% of zinc as naphthenates were added. The following emulsifying agents were used: 1 part of nonaethyleneglycolmonooleate, 2 parts of a condensation product of polyethyleneoxide with higher alcohols, such as oleyl alcohol (a satisfactory product of this type being marketed by the General Dyestuff Corporation under the trade name of Emulphor ON). Both emulsifying agents are non-ionic. To this solution 70 parts of water were added, in which 0.3 part of triethanolamine were dissolved. The mixture was passed through a homogenizer of known design. A fine dispersion of oil in water resulted. The pH of this dispersion was 7.6. This dispersion was too viscous for the treatment with oxygen gas and had to be diluted with 40 parts of water.

Oxygen gas was allowed to pass through this dispersion under a pressure of 2 kg. per sq. cm. and it was found that after 72 hours no more gas was absorbed by the dispersion of the oil. The pH of the oxidized dispersion was 4.8. This dispersion was stable up to a pH of 3.7 and at all hydrogen ion concentrations above pH 7. After evaporation of the water a solid somewhat soft film was left.

Example 2.—100 parts of a dehydrated castor oil was mixed with the usual driers for catalyzing oxidation of the drying oil. As emulsifying agents, 2 parts of a polyethyleneoxide condensation product with castor oil, in nature similar to the polyethyleneoxide condensation product used in Example 1 (a satisfactory product of this type being marketed by the General Dyestuff Corporation under the trade name of Emulphor ELA) and 1 part of a tetrasubstituted ammonium salt of a long chain organic acid and which acts as a cation active product, cetyl dimethyl benzyl ammonium chloride being a satisfactory product of this type (which is also marketed by the Rohm and Haas Company under the trade name of Triton K-60), were used. 100 parts of water containing a very small quantity, about 0.01 part of non ionic surface active agent, was mixed with the oil and the mixture homogenized by mechan-

ical means. A fine dispersion of oil in water resulted with a pH of 6.7. After oxidation in the formerly described manner, the pH was reduced to 4.1. The mixture was stable at pH values of 2 to 10. The particles were migrating in an electrical field toward the negative pole and were positively charged. Above pH 9 the charge was reversed to negative.

Example 3.—100 parts of China-wood oil in which the usual driers were dissolved was used with the following emulsifying or dispersing agents: 2 parts cetyl dimethyl benzyl ammonium chloride, such as used in Example 2, and 2 parts of alkyl dimethyl benzyl ammonium chloride, a quaternary ammonium salt (a suitable product being marketed by the General Dyestuff Corporation under the trade name of Zephiran). Both were dissolved in the oil. 100 parts of water, in which 1 part of hydroxyethylenediamine was dissolved were mixed with the oil and the mixture was homogenized. An oil in water emulsion resulted, with a pH of 8.2. The particles carried a positive charge.

While certain preferred embodiments of the invention have been described hereinbefore, it is to be understood that the invention is not limited to the precise details described and that various changes may be resorted to without departing from the scope of the appended claims.

What is claimed is:

1. A process for preparing a composition of matter comprising a stable aqueous dispersion of an oxidized drying oil, which process comprises emulsifying an oxidizable drying oil in water and subjecting the emulsion to oxidation in the presence of an emulsifying and stabilizing agent, which secures stability of the emulsion at a pH lower than 7 in the presence of acidic by-products formed during oxidation of the drying oil emulsion, the emulsifying and stabilizing ability of said agent being due to another grouping of atoms in the molecule, then to a grouping acting as an anion.

2. A process in accordance with claim 1 in which said agent is a non-ionic agent selected from the class consisting of higher fatty alcohols, polyethyleneoxide condensation products, and esters of long chain fatty acids.

3. A process in accordance with claim 1 in which said agent is a cationic surface active agent incorporating a long chain hydrocarbon radical and a positively charged group selected from the class consisting of sulfonium, pyridinium, phosphonium and quaternary ammonium groups.

4. A process in accordance with claim 1 in which both a non-ionic and a cationic agent is present during oxidation.

5. A process for the preparation and manufacture of emulsions containing oxidized drying oils, consisting in forming an aqueous emulsion containing a drying oil and oxidizing the dispersion in the presence of a cation active emulsifying agent.

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