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EMULSION AND METHOD OF PREPARING SAME

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This invention relates to emulsions and more in particular to the development of stable aqueous wax emulsions which may be employed for sizing of paper or waterproofing of any material in which an increased water resistance may be desired.

In our co-pending applications Serial Nos. 3,807, 9,015, and 13,577, filed January 28, 1935, March 2, 1935, and March 28, 1935, respectively, now matured into Patents No. 2,058,085, October 20, 1936; No. 2,059,464, November 3, 1936, and No. 2,059,465, November 3, 1936, respectively, we have described the application of an emulsion of this nature for beater sizing, tub and calender sizing of paper, and also the pre-sizing of an alkaline earth filler and the application of such a pre-sized filler to produce sized paper. The present invention is a continuation-in-part of Serial No. 3,807 (Patent No. 2,058,085) assigned to the same assignee as the present invention.

Aqueous wax emulsions heretofore available have been found unsatisfactory. For example, the ordinary wax emulsions are unstable in presence of hard water. The tendency of the wax to agglomerate into large particles when subjected to acidic material makes ordinary emulsions unsuited for waterproofing purposes and especially unsuited as a paper size where the wax spots are particularly noticeable.

An object of our invention is to prepare emulsions containing large quantities of wax or waxy material free from the disadvantages enumerated above.

Further objects will be apparent as the description hereinafter proceeds.

We have discovered that waxy material may be dispersed in a stable, finely divided form by emulsifying it with an emulsifying agent such as a soluble soap, provided there is present at the time the wax is being emulsified, a relatively high percentage of protein material. Any protein material which is water-insoluble, acid precipitable but soluble in dilute alkaline solution may be employed, such for example as milk casein or soya bean casein. The emulsions prepared in accordance with our process are highly stable even though the wax content is present in quantities up to 75 percent of solid materials in the emulsion. The wax particles do not agglomerate upon heating neither do they agglomerate due to the hydrolytic action of water nor do they agglomerate in the presence of lime salts in hard water.

To secure the maximum water resistance, the emulsion should be broken by means of an acidic material, but very good water resistance is obtained simply by coating products which are to be waterproofed with the emulsion and removing the water by means of evaporation. While we do not wish to limit ourselves to any particular theory of action, our experimental work indicates that when the emulsion is broken by means of the addition of an acidic material, the minute particles of wax are coated with a molecular film of protein, thus preventing coalescence of these small particles of wax into larger particles.

In case only waterproofing and a slight grease resistance are desired in the material to be treated, an emulsion of approximately 4 parts of wax to 1 part of protein may be employed. In case a higher grease resistance is desired in addition to water resistance, an emulsion of approximately 2 parts of wax to 1 part of protein is employed. These proportions can, of course, be varied to suit the requirements from the standpoint of the relative grease-proofness and waterproofness desired, and the grease- and waterproofness can also be increased by subsequently treating the product which has been waterproofed with an agent which will harden the protein. Such agents are well known in the art, the preferred one being formaldehyde.

Example I

To prepare an emulsion which will give maximum water resistance with some grease resistance, the procedure is as follows: 10 parts by weight of soya bean casein or any other water-insoluble, alkali-soluble protein which can be precipitated from an alkaline solution by means of an acid material such as alum (which eliminates proteins of the nature of glue or gelatine) are heated with 0.7 part of sodium carbonate at approximately 60° C. under mild agitation with 60 parts of water. When the protein is dissolved, 5 parts of any of the well known emulsifying agents such as ammonium oleate, Turkey red oil, soaps of any nature, sulphonated oils, triethanolamine, gums such as gum arabic, or any chemical emulsifying agent are added. The proportion of the emulsifying agent is approximately one-eighth of the amount of wax employed. To this mixture, 40 parts of liquid or molten waxy material are slowly run in under violent agitation, the speed of the agitator varying from 600 to 1750 R. P. M. Any oily or liquid (molten) waxy material such as paraffin may be utilized, the process of emulsification being suitable for emulsifying such oily or waxy materials varying in nature from the very lightest oils available to

materials of the nature of asphalt with melting points of approximately 170° F. It is to be understood that the reference in the chaims to waxy materials is intended to cover mineral, vegetable or animal oily materials which are liquid at room temperature, or solids thereof which have melting points of about 170° F. or less.

The time required for emulsifying the wax is approximately 20 minutes, the emulsification being complete when there is no visible film of oily material on the surface of the mixture. The mixture is then diluted to approximately 10 percent or any other desired percentage at a temperature slightly in excess of the melting point of the oil or waxy material which is being emulsified. Colloid mills or homogenizing equipment might be used in place of high speed stirring, although the high speed stirrer is the preferred method due to simplicity and cheapness.

Example II

In case an emulsion of high water resistance with increased grease resistance is desired, the emulsion is prepared in a manner similar to that described in Example I, except that with the 10 parts of protein dissolved in the 7 percent sodium carbonate solution, 2.5 parts of an emulsifying agent with only 20 parts of wax are employed. Soda ash is the preferred chemical for dissolving the protein because of cheapness, but other alkaline agents such as ammonia, borax, caustic soda, sodium silicate, di-sodium phosphate, or any alkaline material that will dissolve a water-insoluble, acid-precipitable protein may be employed.

The waterproofing agent may be applied by spraying, brushing, dipping, or any other well known method of application. In case maximum water resistance is required, as in the case of textiles, the material to be treated is first run through a 2 percent solution of alum, to which is added 5 percent of formaldehyde calculated on the weight of the alum, the excess solution being removed from the material by squeezing. The material is then run through the bath of the emulsion and again squeezed to remove the excess of emulsion. The reverse treatment, of course, may also be used, whereby the emulsion is applied first and then set by means of alum. The function of the formaldehyde is to harden the protein and render it more insoluble.

Our emulsion may be used for a variety of purposes, such as the sizing of paper, the waterproofing of textiles, felt, furs, hair, straw, or feathers; the waterproofing of cement, stucco, plaster, or composition blocks; and the waterproofing of leather, board, lumber, or any product in which an increase of water resistance or the prevention of warping through moist atmospheric conditions might be desirable. We have found, for example, that very porous building materials such as plaster walls, building board or similar material, when primed with a coat of our improved emulsion, can be painted satisfactorily with several less coats of paint than are required for the uncoated material, due to the fact that the paint lies on the surface of the coated material rather than penetrating into the board. Cement tanks, for example, to be made resistant to the action of alum or any other relatively mild corrosive agent, may be treated by this inexpensive method to render the surface of the tank impervious to the action of the corrosive liquid. Furthermore, such a treatment may be given at intervals by means of a spray gun at very little expense in a relatively short time.

In general, the best results are secured by having as viscous an emulsifying medium consisting of the alkaline protein solution and the emulsifying agent as is consistent with vigorous agitation. This can best be controlled by varying the temperature or the amount of water used, which, in turn, will depend to a great extent upon whether the emulsion is to be prepared with a material like oil which is a liquid at room temperature, with a wax having a melting point of about 120° F., or with a material of a higher melting point such as an asphalt.

While we have illustrated our invention with certain specific examples, it is to be understood that our invention is not limited thereto. All modifications coming within the true spirit and scope of our invention are meant to be covered by the appended claims.

We claim:

1. The method of preparing stable emulsions which comprises adding a liquid waxy material accompanied by agitation to an aqueous alkaline solution containing a water-insoluble, acid-precipitable protein and an emulsifying agent, said emulsion being stable in the presence of hard water and said protein being present in such quantity relative to the waxy material that the particles thereof are surrounded by a protein film preventing agglomeration of the waxy particles when the emulsion is broken by addition of acidic material, the ratio of protein to waxy material being at least about 1:4.

2. The method of preparing stable emulsions comprising a liquid waxy material accompanied by agitation to an aqueous alkaline solution containing milk casein and an emulsifying agent, said casein being present in such quantity relative to the waxy material that the particles thereof are surrounded by a protein film preventing agglomeration of the waxy particles when the emulsion is broken by addition of acidic material, the ratio of casein to wax being at least about 1:4.

3. The method of preparing stable emulsions comprising adding a liquid waxy material accompanied by agitation to an aqueous alkaline solution containing soya bean casein and an emulsifying agent, said casein being present in such quantity relative to the waxy material that the particles thereof are surrounded by a protein film preventing agglomeration of the waxy particles when the emulsion is broken by addition of acidic material, the proportion of ingredients in the emulsion being such that the protein content is at least about 25 percent as great as the wax content.

4. The method of preparing stable emulsions comprising adding about four parts of a liquid waxy material accompanied by agitation to an aqueous alkaline solution containing from about one to two parts of a water-insoluble, acid-precipitable protein and an emulsifying agent.

5. The method of preparing stable emulsions comprising adding about eight parts of a liquid waxy material accompanied by agitation to an aqueous alkaline solution containing about two to four parts of a water-insoluble, acid-precipitable protein and about one part of an emulsifying agent.

6. The method of preparing stable emulsions comprising adding molten paraffin accompanied by agitation to an aqueous alkaline solution containing a water-insoluble, acid-precipitable pro-

tein and an emulsifying agent, said protein being present in such quantities relative to the paraffin that the particles thereof are surrounded by a protein film preventing agglomeration of the paraffin particles when the emulsion is broken by the addition of acidic material, the ratio of protein to paraffin being at least about 1:4.

7. The method of preparing stable emulsions comprising adding molten paraffin accompanied by agitation to an aqueous alkaline solution containing soya bean protein and ammonium oleate, said protein being present in such quantity relative to the paraffin that the particles thereof are surrounded by a protein film preventing agglomeration of the paraffin particles when the emulsion is broken by the addition of acidic material, the emulsion on a dry basis containing at least about 18 percent protein and the ratio of protein to paraffin being at least about 1:4.

8. The method of preparing stable emulsions comprising adding liquid waxy material accompanied by agitation to an aqueous alkaline solution containing milk casein and an emulsifying agent, said emulsion comprising about eight parts waxy material, about two to four parts casein and about one part emulsifying agent.

9. An emulsion comprising waxy material stabilized by an aqueous alkaline solution containing a water-insoluble, acid-precipitable protein and an emulsifying agent, said emulsion being stable in the presence of hard water and said protein being present in such quantity relative to the waxy material that the particles thereof are surrounded by a protein film preventing agglomeration of the waxy particles when the emulsion is broken by addition of acidic material, the ratio of protein to waxy material being at least about 1:4.

10. An emulsion comprising waxy material stabilized by an aqueous alkaline solution containing milk casein and an emulsifying agent, said casein being present in such quantity relative to the waxy material that the particles thereof are surrounded by a casein film preventing agglomeration of the waxy particles when the emulsion is broken by addition of acidic material, the ratio of casein to wax being at least about 1:4.

11. An emulsion comprising waxy material stabilized by an aqueous alkaline solution containin soya bean casein and an emulsifying agent, said casein being present in such quantity relative to the waxy material that the particles thereof are surrounded by a casein film preventing agglomeration of the waxy particles when the emulsion is broken by addition of acidic material, the proportion of ingredients in the emulsion being such that the casein content is at least about 25 percent as great as the wax content.

12. A stable emulsion comprising an emulsifying agent, about four parts of waxy material and about one to two parts of a water-insoluble, acid-precipitable protein dissolved in an aqueous alkaline solution.

13. A stable emulsion comprising about one part of an emulsifying agent, about eight parts of waxy material and about two to four parts of a water-insoluble, acid-precipitable protein dissolved in an aqueous alkaline solution.

14. A stable emulsion comprising paraffin, an aqueous alkaline solution containing a water-insoluble, acid-precipitable protein and an emulsifying agent, said protein being present in such quantity relative to the paraffin that the particles thereof are surrounded by a protein film preventing agglomeration of the paraffin particles when the emulsion is broken by addition of acidic material, the ratio of protein to paraffin being at least about 1:4.

15. A stable emulsion comprising waxy material, an aqueous alkaline solution containing milk casein and an emulsifying agent, said emulsion comprising about eight parts waxy material, about two to four parts casein, and about one part emulsifying agent.

16. A stable emulsion comprising paraffin, an aqueous alkaline solution containing soya bean protein and ammonium oleate, said protein being present in such quantity relative to the paraffin that the particles thereof are surrounded by a protein film preventing agglomeration of the paraffin particles when the emulsion is broken by addition of acidic material, the emulsion on a dry basis containing at least about 18 percent protein and the ratio of protein to paraffin being at least about 1:4.

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CERTIFICATE OF CORRECTION.

Patent No. 2,172,392. September 12, 1939.

OTTO KRESS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 3, Example 1, for "chaims" read claims; and second column, line 36, claim 2, after the word "comprising" insert adding; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of November, A. D. 1939.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.