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SIZING PAPER

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Our invention relates to the sizing of paper with paraffin or the like, and may be considered as another method of utilizing the improved sizing composition described and claimed in our co-pending applications Serial Nos. 3,807 and 9,015, filed January 28, 1935, and March 2, 1935, respectively. In said application Serial No. 3,807 we describe and claim an improved highly stable emulsion of colloidally-dispersed paraffin protected by means of a protein, such as soya bean or milk casein, and containing an emulsifying agent, such as a soap or Turkey red oil, etc. We also describe and claim in said application a method of utilizing said size in paper making by applying the same to the fiber in the furnish. In application Serial No. 9,015 a similar size is applied to an alkaline filler.

We have also found that such a colloidally-dispersed paraffin size composition may be utilized to advantage by applying the same to a formed sheet of paper, or in process of formation, in accordance with any known or suitable method of applying size to a paper web. We find that such material may be applied to either a wet or dry sheet in accordance with standard practice, and results in a highly improved sheet of paper.

An object of our invention, accordingly, is to provide an improved method of the type referred to.

Still another object is to provide an improved paper product, made according to said method, which is highly impervious to water and oil and which is of special value as a wrapper or container, especially for foodstuffs, etc.

Various other objects and advantages will become apparent as the description proceeds.

We are aware that various attempts have been made to use paraffin, wax, and similar material as a sizing agent, and endeavors have also been made to provide emulsions of such material. However, all of said emulsions with which we are familiar have the very serious drawback that, if they contain any substantial percentage of waxy material, the emulsion is likely to break, with the consequent agglomeration of the wax particles, producing wax spots on the paper machine or in the finished paper.

In contradistinction to such prior efforts, our improved emulsion, wherein the waxy material is protected by means of a protein, such as soya bean or milk casein, and containing an emulsifying agent, such as ammonium oleate or other suitable emulsifier, is highly stable for long periods of time, resisting elevated temperatures, shock, and chemicals, except acidic materials, and, when set, will deposit the wax in finely-divided colloidal form, the particles of wax being surrounded by a protein film so as to produce a perfectly sized sheet free from wax spots. In accordance with our invention, therefore, agglomeration of the wax particles either on the wire or sheet is prohibited, thus obviating both troublesome filling in of the wire and unsightly wax spots in the finished paper.

In accordance with the method forming the subject-matter of the present application, our improved size is applied to the sheet after the latter is formed, or during the formation, either on a cylinder machine or on a Fourdrinier type of machine. There may also be added to the stock such ingredients as starch, color, etc., as are usually added to a paper mix.

Example of size composition

As fully described in our co-pending applications, above referred to, our improved size comprises a waxy material, such as paraffin, stabilized by means of a protein, such as milk casein or soya bean casein, together with an emulsifying agent, such as a soap or Turkey red oil. The following is a preferred example of a composition applicable to the manufacture of a sheet especially suitable for butchers' paper, bread wrap, cracker wrap, drinking cups, etc.

To 10 parts of casein are added 0.7 part of sodium carbonate and the material is heated to about 60° C. under mild agitation with about 60 parts of water. To this are added 5 parts of ammonium oleate, although various other emulsifying agents may be used, such as Turkey red oil, gum arabic, sodium stearate, etc. To this mixture are slowly run in under agitation about 40 parts of paraffin wax having a melting point of about 122° F., although paraffins having lower or higher melting points, or even materials which are oils at ordinary temperatures, may be employed. This provides a mixture consisting of approximately 72.5 per cent of wax and 18.2 per cent of casein. It will be understood, of course, that these proportions may be varied within wide limits. If it is desired to produce a paper of good-moisture resistance and at the same time of high strength, we have found that a mixture consisting of 15 parts of protein, 2.5 parts of ammonium oleate, and 30 parts of paraffin wax give excellent results, such a mixture providing on a dry basis 63 per cent paraffin and 31.6 per cent casein. Of course, these proportions may be varied considerably, depending upon the strength of the paper desired and the water and blood re-

sistance desired in the finished paper. It will be apparent to one skilled in the art that as the quantity of waxy or oily material is varied sufficient protein must be employed to coat the wax particles with a protein film when the emulsion is set, as described below, in order to prevent coalescence of the wax particles to form large paraffin masses which will offer difficulty on the paper machine or in the finished paper. The mixture of ingredients described above is stirred with a high-speed stirrer or other suitable equipment. The time of mixing is, say, about 15 minutes, the mixture then being diluted with 1000 parts of water at approximately 60° C., although the temperature may be varied, depending upon the melting point of the paraffin being used. The emulsion may also be made through the use of a colloid mill or other suitable equipment.

One obvious benefit resulting from the increase in the proportion of casein, through which increased strength is obtained, is that the paper mix need not be treated to the same mechanical degree by beating, jordaning, etc., with the result that the paper produced will be more opaque, longer fibered, and for certain purposes more desirable than stock which has been hydrated to a greater degree by such mechanical means. Moreover, the strength of the sheet will be at least equivalent to the strength of stock hydrated to a greater degree, and for practical purposes the sheet will be a stronger one in view of the action of the casein in binding together the individual fibers of the sheet. It is well known in the paper art that stock which has been mechanically treated more severely to develop the physical strength of the finished sheet will dewater more slowly on the paper machine and will dry with more difficulty; as a result, the speed of the machine must be reduced. We thus find it possible by this means to produce a cheaper paper with the desirable characteristics of a more expensive sheet.

Application of the size

One method of applying this emulsion that we employ very successfully is with the use of an ordinary size press, as follows: The paper mix is put over the paper machine in the usual manner, and the sheet is dried in the customary way by passing the wet sheet over the drier section of the paper machine. The dried paper then passes between two squeeze rolls running in a bath of our emulsion as described above, or the emulsion may be pumped by well known means through suitable spray pipes to the top nip of the roll and onto the bottom roll, thereby incorporating the emulsion into the paper, which is then dried according to standard paper-making practice over additional driers, after which it may be calendered, if desired, and wound into finished rolls. If it is desired to coat only one side of the sheet, which may be either the top or bottom, we employ only one spray, thereby introducing the emulsion to but one side of the paper.

In admixture with the emulsion described above we can introduce fillers or opacifying pigments, thereby producing an opaque sheet of paper at a low cost. To soften the sheet, we may introduce softening agents, such as invert sugar, in admixture with the emulsion, adding from 3 to 5 per cent glucose, depending upon the degree of softening desired. To color the sheet, we have demonstrated that we can, by the addition of suitable aniline colors to the wax emulsion, coat one or both sides of the paper to produce any desired shade by this means. The actual mechanical operation is according to standard paper making methods, in which the emulsion, say at 10 per cent total solids concentration and temperature of 60° C., is placed in a suitable tank from which it is pumped to the size press, the excess returning by means of a suitable overflow to the storage tank.

To render ordinary board such as chip board, container board, or any board product waterproof, the emulsion is introduced on the so-called water boxes of the calender stack, and here, again, we may introduce other materials, such as filler, color, starch, or any of the well-known paper-making constituents that are used to secure certain characteristics in the finished sheet, these materials being admixed in suitable proportion with the stabilized emulsion.

As already mentioned, for the ordinary flat pass size press or for the water boxes on the cylinder board machine, we prefer to use an emulsion of about 10 per cent total solids concentration, but this concentration may be varied, depending upon the speed of the machine, the temperature of the emulsion, and the amount of solids which we desire to incorporate into the finished paper. With the ordinary flat press, where the paper is not submerged in the bath and where all of the emulsion is applied in the form of sprays at the nip of the size press rolls, we prefer to use a 10 per cent concentration, which will introduce from 1.5 to 5 per cent of solids into the sheet, this largely depending upon the weight of the paper, speed of the press, and also upon whether or not the paper has been pre-sized, and the degree thereof. Naturally, this emulsion can be applied in the form of a spray after the sheet has been formed on either the Fourdrinier or cylinder type of machine and may also be applied by suitable carrying rolls at the wet end of the machine, all according to standard mill technique.

In accordance with the methods described herein, the usual alum-rosin size will have been introduced into the beater or the stock will have been sized with the stabilized wax emulsion as described in our co-pending application Serial No. 3,807, filed on January 28, 1935, so that the stock is acid, and the wax emulsion is set by means of the residual alum in the sheet, an excess of which is normally present in the finished sheet of paper. Obviously, other acidic setting agents may be employed.

Summarizing, our improved size may be applied to the web in a size press on a paper machine, in water boxes in the case of a board machine after the sheet has been formed and dried, or by applying the emulsion at the wet end of a paper machine as by means of suitable carrying rolls, sprays, etc. In any event, standard paper-making technique and equipment are employed.

Where it is desired to size alkaline earth filled papers, such paper is run over the paper machine in a slightly alkaline condition, as no sizing will have been employed and alkalinity is produced through the use of the alkaline-earth fillers. We have found that ample sizing for commercial purposes can be produced on the size press with the stabilized wax emulsion.

Under such conditions, we do not believe that the stabilized emulsion is decomposed or set, as does happen when the sheet is slightly acid, but apparently a waterproof film is produced mechanically when the paper is dried by simple dep-

osition of the solids which have been suspended in the emulsion in the size press.

Waterproofing of finished papers

An important application of our invention lies in the waterproofing of finished papers, such as, for example, wall paper, there being at the present time a high demand for washable wall paper. Papers may be treated in accordance with our invention by applying to one or both surfaces thereof our improved size emulsion in any of the ways described above. Normally, such papers will contain sufficient free alum to set the emulsion.

Various other embodiments and various modifications coming within the spirit of our invention will no doubt suggest themselves to those skilled in the art. Hence, we do not wish to be limited to the specific details set forth herein, but intend that the scope of our invention is to be determined from the appended claims, which should be interpreted as broadly as is consistent with the state of the art.

We claim as our invention:

1. The method of manufacturing paper comprising forming a paper web, applying to said web an aqueous colloidal dispersion of waxy material stabilized with a water insoluble protein, the latter being present in such a quantity relative to the wax that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles, said web containing an acidic substance which will react with the dispersion and fix the particles of waxy material on the web fibers.

2. The method of manufacturing paper comprising forming a paper web, applying to said web an aqueous colloidal dispersion of waxy material stabilized with a member of the group consisting of milk casein and soya bean casein, said stabilizer being present in such a quantity relative to the wax that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles, said web containing an acidic substance which will react with the dispersion and fix the particles of waxy material on the web fibers.

3. The method of manufacturing paper comprising forming a paper web, and applying to said web an aqueous colloidal dispersion of waxy material stabilized with a quantity of the order of 25 to 50%, based on said waxy material, of a member of the group consisting of milk casein and soya bean casein, said stabilizer functioning to prevent agglomeration of the wax particles, and said web containing an acidic substance which will react with the dispersion and fix the particles of waxy material on the web fibers.

4. The method of manufacturing paper comprising forming a paper web which is acid in reaction, and applying to said web an aqueous colloidal dispersion of paraffin stabilized with a member of the group consisting of milk casein and soya bean casein, said stabilizer being present in such a quantity relative to the paraffin so that the particles of paraffin deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the paraffin particles, said paraffin being set by the acid to size the web.

5. The method of manufacturing paper comprising forming a paper web which is acid in reaction, applying to said web an aqueous colloidal dispersion of waxy material stabilized with a member of the group consisting of milk casein and soya bean casein, said stabilizer being present in such a quantity relative to the wax that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles, said waxy material being set by the acid to size the web.

6. The method of manufacturing paper comprising forming a paper web which is acid in reaction, and applying to said web an aqueous colloidal dispersion of waxy material stabilized with a qantity of the order of 25 to 50%, based on said waxy material, of a member of the group consisting of milk casein and soya bean casein, said stabilizer functioning to prevent agglomeration of the wax particles, said waxy material being set by the acid to size the web.

7. The method of manufacturing paper comprising applying to a web of paper containing an alkaline earth filler a size comprising an aqueous colloidal dispersion of waxy material stabilized with a water-insoluble protein, the latter being present in such a quantity relative to the wax so that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles and drying the web.

8. The method of manufacturing paper comprising applying to a web of paper containing an alkaline earth filler a size comprising an aqueous colloidal dispersion of waxy material stabilized with a member of the group consisting of milk casein and soya bean casein, the latter being present in such a quantity relative to the wax, so that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles and drying the web.

9. The method of manufacturing paper comprising applying to a web of paper containing an alkaline earth filler a size comprising an aqueous colloidal dispersion of waxy material stabilized with a quantity of the order of 25 to 50%, based on said waxy material, of a member of the group consisting of milk casein and soya bean casein, the latter being present in such a quantity relative to the wax, so that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles and drying the web.

10. A method comprising applying to a web of paper containing an alkaline earth filler, at the size press, a size comprising an aqueous colloidal dispersion of waxy material stabilized with a water-insoluble protein, the latter being present in such a quantity relative to the wax that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles and drying the web.

11. A method comprising applying to a web of paper containing an alkaline earth filler, at the size press, a size comprising an aqueous colloidal dispersion of waxy material stabilized with a member of the group consisting of milk casein and soya bean casein, the latter being present in such a quantity relative to the wax that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles and drying the web.

12. A method comprising applying to a web of paper containing an alkaline earth filler, at the size press, a size comprising an aqueous colloidal dispersion of waxy material stabilized with a quantity of the order of 25 to 50%, based on said waxy material, of a member of the group consist-

ing of milk casein and soya bean casein, the latter being present in such a quantity relative to the wax that the particles of wax deposited on the web are surrounded by a protein film, thereby preventing agglomeration of the wax particles and drying the web.

13. The method of manufacturing paper comprising applying to the finished paper a colloidal aqueous dispersion of finely divided waxy material containing and stabilized by a water insoluble protein in such quantity as to protect and maintain the waxy material in finely divided colloidal form, and drying to produce a sized sheet free from wax spots.

14. The method of manufacturing paper comprising applying to the finished paper a colloidal aqueous dispersion of finely divided waxy material containing and stabilized by a water insoluble alkali soluble protein in such quantity as to protect and maintain the waxy material in finely divided colloidal form, and drying to produce a sized sheet free from wax spots.

15. The method of manufacturing paper comprising applying to paper containing an acidic constituent, a colloidal aqueous dispersion of finely divided waxy material containing and stabilized by a water insoluble protein in such quantity as to protect and maintain the wax in finely divided colloidal form, and drying to produce a sized sheet free from wax spots.

16. The method of manufacturing paper comprising applying to finished paper containing an alkaline earth filler, a colloidal aqueous dispersion of finely divided waxy material containing and stabilized by a water insoluble alkali soluble protein in such quantity as to protect and maintain the waxy material in finely divided colloidal form, and drying to produce a sized sheet free from wax spots.

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