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COATED PAPER

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14 Claims. (Cl. 91—68)

This invention relates to a coated material, and while the invention comprehends various forms of coated material having diverse uses, one form which is especially useful is a coated sheet material suitable for packaging.

In packaging goods for the market, it is the object of the merchant to provide an inexpensive, attractive, distinctive package, and in most cases and particularly in the packaging of foods, tobacco and like products which absorb moisture, it is necessary to protect the packaged goods from the atmospheric moisture as well as the dust and dirt. This desideratum has not, however, heretofore been attainable with a single wrapping. Each factor, the attractive, distinctive appearance of the package and the resistance to penetration of the atmospheric moisture, has required a separate and distinct wrapping paper. In practically all cases a printed design is used to make the package attractive and distinctive and usually the papers which are somewhat impervious to moisture are not suitable for printing. Another wrapper is therefore used to exclude moisture; in some cases an inner wax paper is used, and in other instances an outer, moisture-proof, transparent, regenerated-cellulose sheet wrapper is used.

By this invention, a coated sheet may be produced which is suitable for printing, which has an exceptionally attractive surface and which is impervious to moisture. Thus, the desirable qualities of an attractive, distinctive package may be obtained with a single wrapping. The surface of the coated sheet of this invention includes such characteristics as a very smooth, highly polished surface similar in all respects to the surface of a photograph and when in the process of making the sheet, the coating is applied after printing, the brilliance, and depth of tone of the printed image are materially enhanced and simulate the depth of tone and brilliance of a photograph. A non-tacky surface, and a surface which is not affected by normal atmospheric conditions are also properties of a coated sheet embodying this invention. Such a coated sheet is made in accordance with this invention by utilizing, in conjunction with a sheet which is substantially impervious to moisture, a coating of composition which comprises a film forming colloid having in intimate moisture, a coating composition which compound which repels moisture and which in the dried and polished state, prevents atmospheric moisture from permeating the coating and destroying either the smoothness, polish or non-tacky nature of its surface. The insoluble compound is so introduced into the film forming colloid that it is in a fine state of dispersion throughout the colloid.

A coated paper suitable for a wrapper and embodying this invention may be made by a method which forms a part of the invention. The method which is especially applicable to moisture-pervious paper such as the paper commonly used as label paper includes three operations which are performed upon the paper, sizing, coating and glossing or polishing. If a design is to be printed on the paper, the printing may be done either before or after the sizing operation, preferably after. The paper is sized with a water-insoluble size containing a water-insoluble soap, particularly a water-insoluble metallic soap, such as aluminum oleate, zinc oleate, lead oleate, magnesium oleate and the like, a wax, such as paraffin, beeswax, carnauba, china, etc., and a fatty acid, particularly a saturated or unsaturated fatty acid containing ten carbon atoms or more such as linoleic, ricineoleic, stearic or oleic acid. The functions of the size are to increase the moisture-resistance of the sheet, that is, the resistance of the sheet to penetration by moisture, to increase the flexibility of the sheet, to prevent the coating, subsequently applied, from entering into the fibers of the paper and to provide a favorable anchorage for the coating film. The size imparts these several properties to the paper without discoloring the paper, which is one of the detriments of ordinary sizing agents.

While it is possible to size the paper in the ordinary way, that is, by precipitating the size on the fibers in the furnish, I prefer to use a process commonly known as surface sizing in which a solution of the size in a solvent is applied to the finished paper by drawing the paper through the solution. A solution which I find particularly suitable for the purpose of the coated sheet of this invention, includes one part of aluminum oleate, one part of paraffin, and one-half part of oleic acid, dissolved in carbon-tetrachloride. The volume of the carbon-tetrachloride which I have found suitable is approximately 7 to 45 cc. for every gram of aluminum oleate. Any of the low boiling, non-corrosive hydrocarbons or chlorinated hydrocarbons, such for example as tetrachlorethylene, can be substituted for the carbon-tetrachloride as the solvent. The mechanical operation of sizing is similar to the ordinary well known tub sizing. A quantity of the sizing solution is placed in a suitable container and the paper to be sized is drawn through

the solution and passed through a pair of rollers to remove the excess sizing solution. The solvent is evaporated from the sheet leaving the size in the sheet in the form of a thin film. The solvent may be recovered in the drying operation and re-used. After the solvent is removed from the paper, the paper is coated.

The surface of the sized paper is coated with a film forming colloid which forms a transparent film on the surface of the paper. The coating composition used is similar to the coating composition of the copending Boyce application Serial No. 545,833, filed June 20, 1931. The coating herein described, however, differs from the coating of the Boyce application in that it is not affected by moisture. The gelatin film forming colloid of the Boyce application produces a film on the surface of a paper which is moderately moisture-resistant but which when exposed to a humid atmosphere takes up moisture and becomes somewhat tacky. After long exposure to 100° F. and an atmosphere containing 100% humidity, the film in some cases becomes actually soggy. In the film forming composition which is used to form the coated sheet of this invention, these disadvantages are eliminated. This film forming composition forms the subject matter of a copending divisional application Serial No. 680,975, filed July 18, 1933, and includes, initially, a film forming emulsion having an insoluble compound in intimate admixture therewith. In preparing the film forming coating composition, a film forming emulsion is made. To this emulsion a quantity of a water-soluble salt, particularly a water-soluble salt of any of the metals other than the metals of the first group of the periodic system, is added and intimately mixed with the emulsion. Barium and calcium salts, particularly the chlorides and nitrates, are especially suitable. These salts are dissolved in the emulsion and there is then added a solution of a sulphonated oil. This solution of a sulphonated oil reacts with the water-soluble metallic salt and produces a sulphonated oil compound which is virtually insoluble in water. In the presence of the gelatin the insoluble sulphonated oil compound that is produced by the reaction of the sulphonated oil with the water-soluble metallic salt, is in an exceedingly fine state of dispersion and is not precipitated as coarse coalescing globules which would be the case in the absence of the emulsion.

One specific form of the coating composition which is suitable for coating paper is compounded in the following manner, the quantities of the ingredients being merely illustrative: 32 gms. of gelatin are swelled by letting the gelatin soak in 180 cc. of water for a period of twelve hours. The swelled gelatin is heated in a water bath to 120° F. and while in a liquid state, 1 cc. of 50% acetic acid is added. At this time, a solution of calcium nitrate is added, the solution of calcium nitrate being made by dissolving crystallized calcium nitrate in water. The quantities of water and nitrate used are adapted to produce a solution of 1 gm. mole per liter. Other soluble salts of the alkaline earths, such as calcium chloride, calcium acetate, and similar barium salts, are equally suitable.

As heretofore stated, the water-soluble metallic salt reacts with a sulphonated oil which is added to the mixture after the addition of the solution of calcium nitrate. In the case being described, 14 cc. of molar calcium nitrate solution would be added to the gelatin acetic acid mixture. In any solution, the proper amount of the calcium nitrate solution to be added can be determined in the following manner: 22 gms. of the sulphonated and neutralized castor oil, hereinafter more particularly described, are diluted with about 50 cc. of water in a small Erlenmeyer flask, provided with a cork. The calcium nitrate solution is placed in a burette and added to the solution of the sulphonated oil, one-half cc. at a time. The flask is shaken vigorously after each addition of calcium salt solution, to cause foaming. It will be found that the addition of approximately 15 cc. of the calcium salt solution will practically stop all foaming. This volume is read accurately and represents a measure of the calcium solution necessary to precipitate completely the sulphonated oil. From 90 to 95% of this quantity of calcium nitrate solution is then added in the coating solution.

The next step is the addition of the sulphonated oil. The substance here designated as the sulphonated oil is a sodium neutralized sulphonated oil; for the purpose of the specific composition being described, it is the sodium neutralized product of the reaction of 30% by weight of concentrated sulphuric acid (O. V.) and 70% by weight of castor oil. The reaction is carried out at a temperature below 35° C. and requires approximately five hours. Such a sulphonated mass contains about 8.5% combined sulphur-trioxide SO_3. This product is washed by adding to it an equal quantity of water, thoroughly stirring the mixture and letting it settle. The water is then drawn off and the sulphonated mass is neutralized with the proper quantity of caustic soda, 32° Bé. Any other sulphonated oil, such for example as olive oil, is suitable for the purpose, but a sulphonated castor oil is preferred.

In the example being given 22 gms. of the sulphonated mass are added to 20 cc. of water and the mixture is added to the gelatin mixture. The result of the addition of the sulphonated mass is the production in the mixture of the insoluble calcium salts and also of the separation of the free castor oil in the sulphonated oil, in an extremely fine state of dispersion throughout the gelatin. The gelatin, and a small quantity of the remaining sodium salt of sulphonated oil act as protective colloids to maintain the fine state of division of the oil and calcium salts. The same result can be obtained from the reaction of the sodium neutralized sulphonated oil with a soluble salt of any of the following metals: strontium, barium, zinc, cadmium, mercury, lead, aluminum, glucinum, tin, bismuth, etc.

After the sulphonated mass has been added the following are added successively: a mixture of 150 cc. of water and 7 cc. of butyl alcohol, a mixture of 1.25 cc. of ammonia, 4.25 cc. of a 5% solution of phenol in water, and 20 cc. of water, a mixture of 2.5 cc. of a 40% solution of formaldehyde and 45 cc. of water, and 100 cc. of water. The butyl alcohol apparently serves two functions. During the coating process, it lowers the surface tension of the water and thus promotes a spreading of the composition; it also aids in tying the film to the sized paper, acting as an additional bonding link between the paper and the coated film. Any one of the three isomers of butyl alcohol, primary, secondary or tertiary or mixtures, may be used.

The formaldehyde serves to harden the gelatin; it is not an essential ingredient and can be dispensed with. However the small quantity of formaldehyde mentioned seems to produce a

firmer film which has less tendency to squeeze off in the enameling or polishing operation which will hereinafter be described.

The phenol (carbolic acid, U. S. P.) is simply a preservative. Beta naphthol or any other good preservative, which will prevent bacterial growth, may be substituted for the phenol.

Any other suitable soluble organic acid can be substituted for the acetic acid. The acetic acid is merely used to assist in the action of the water on the gelatin.

It has been found that the clearness and resistance to penetration by moisture are appreciably increased by using a sulphonated castor oil which has been freed as nearly as possible from inorganic salts (especially sodium sulphate). The sulphonated oil can readily be freed from these soluble salts by making a solution of the sulphonated oil with an equal volume of acetone, letting the solution stand over night to allow the salts to crystallize, and then filtering to remove the salts after which the acetone may be evaporated.

When the film forming coating composition is made as described above, certain soluble salts are produced in the double decomposition such, for example, as sodium nitrate. While these soluble salts are undesirable it is quite probable that they are immaterial in the small quantities in which they are present in the film forming coating composition. The production of these soluble salts may however, be reduced to a minimum in the preparation of the film forming composition by the method described below. This latter method is also less expensive than the former and it involves materials which are less costly, and saves the work of certain intermediate steps. As before, 32 gms. of gelatin are soaked in 180 gms. of water for a period of twelve hours. The gelatin is then heated in a water bath to 120° F. and 1 cc. of a 50% acetic acid is added. Thereafter a quantity of calcium oxide, previously slaked in water, not quite sufficient to neutralize the sulphonated mass to be later added, is then added to the mixture.

The amount of calcium oxide to be added may be determined in the following manner: A portion of the sulphonated mass, hereinafter described, is weighed and diluted with cold water. The mass is then titrated at once with standard sodium hydroxide solution. From the results of this titration the quantity of calcium oxide necessary for complete neutralization is readily calculated. Between 90 and 95% of the calculated quantity of calcium oxide is weighed out, ground in a mortar, slaked with water and then added to the gelatin which has been warmed to 120° F. In addition 1 cc. of concentrated ammonium hydroxide is added at this time. To the quantity of water-soaked gelatin described above, the following are added: 1 gm. of calcium oxide is added together with 50 cc. of water and 1 cc. of ammonia.

The sulphonated mass referred to above and which is used in this specific form of the composition and which is now added to the mixture is the unneutralized product of the reaction of 30% by weight of concentrated sulphuric acid (O. V.) and 70% by weight of castor oil. The reaction is carried out at a temperature below 35° C. and requires approximately five hours. In this method, as in the one previously described, any other sulphonated oil may be used but sulphonated castor oil is preferred.

During the addition of the sulphonated mass, the gelatin solution is stirred vigorously. In the illustrative case, a mixture of 22 gms. of the sulphonated mass and 50 cc. of water are added to the gelatin solution. When the addition of the sulphonated mass is complete, the solution is tested with litmus paper and if necessary it is neutralized. If the solution is found to be acid, ammonia is added to bring it to neutrality; if it is alkaline, acetic acid is added. When the solution has been made neutral, the following mixtures are added successively: 7.5 cc. of butyl alcohol, 4.5 cc. of phenol, 50 cc. of water; 1.25 cc. of ammonia and 10 cc. of water; and, 45 cc. of water and 2.5 cc. of formaldehyde. Finally, there are added 100 cc. of water. The composition so formed is ready to be applied to the paper and should be applied at once.

Strontium hydroxide or barium hydroxide and the like may be substituted for the calcium oxide used in this formula.

The coating composition which is in the form of an emulsion is applied to the surface of a paper in the usual and well known manner. It is preferably done with the reverse roller coating machine as this produces a very uniform coating. After the sheet is coated, it is dried. The dried coating is then polished or glossed. This polishing applies a high gloss to the coated surface and gives the surface the appearance of a photographic gelatin film. This polishing operation consists in moistening or wetting the coating on the paper and in the wet or moist condition firmly pressing the surface of the coating against a highly polished surface such as a chromium or nickel surface warmed to approximately 110° F. The sheet pressed against this chromium surface is kept in contact with the chromium surface until the gelatin sets, after which the sheet is removed. The chromium surface may preferably be in the form of a cylinder and the sheet is pressed against this cylinder.

The solution used in wetting the coating of the paper includes 21 gms. of gelatin, 3½ gms. of sulphonated castor oil, 2 cc. of butyl alcohol and 200 cc. of water. The gelatin is soaked in the water for a few minutes and then an additional 200 cc. of warm water is added. Just prior to wetting the surface of the paper with this solution, 7 cc. of formaldehyde in 200 cc. of water are added to the solution. The solution is warmed to about 80 to 90 degrees F. and in this heated condition it is applied to the surface of the paper. Like the coating, this wetting solution may be applied to the coated surface by a reverse roller.

In the dried, hardened gelatin composition it is believed that the gelatin forms a strong sponge-like structure and the voids of the sponge-like structure are filled with the free castor oil and the insoluble calcium salts of the sulfonated oil. The castor oil and the insoluble calcium compound serve essentially two purposes; they render the film highly moisture-resistant and they give it flexibility. The calcium compound, being insoluble in water, will not tend to swell by taking up moisture and it serves to prevent moisture from penetrating into the composition. It is quite probable that the hardened gelatin structure is extensively coated by the oily material separated from the sulphonated oil. This coating repels moisture and prevents wetting of the gelatin structure by moisture. The oil further serves as a link of adhesion between the dried emulsion and the aluminum oleate in the sizing with which the paper was sized. The finished sheet also has an exceptionally high resistance to penetration by oil.

The finished coated paper has a very high gloss.

If it is a paper on which a printed design is formed and the coating is put on after the printing, the coating is left in its natural condition and forms a highly polished, transparent film on the surface of the paper which materially enhances the brilliance and depth of tone of the printed image. Very beautiful effects may also be obtained by adding dyes and metallic powders such as the common aluminum and bronze powders to the emulsion before it is applied to the paper. The combined action of the size and the coating renders ordinary paper practically impervious to moisture.

While the embodiment of the invention described in detail above is specific to ordinary paper, various other fibrous and non-fibrous sheet material is suitable as a base. For example, a sheet of transparent, regenerated cellulose may be coated as herein described and when so coated it is highly resistant to moisture penetration, non-tacky and unaffected by ordinary atmospheric conditions.

By the term sheet as used herein I do not intend to distinguish between a web of material but intend the term to be generic to sheet material whether in the form of a continuous web or cut into sheets.

It is obvious that various changes may be made by those skilled in the art in the details of the embodiments of the invention as described above within the principle and scope of the invention as expressed in the appended claims.

I claim:

1. A decorative coated sheet material including a base and a coating on the surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and a water-insoluble salt of a metal other than a metal of the first group of the periodic system in a fine state of dispersion throughout the composition.

2. A decorative coated sheet material including a base and a coating on a surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and a water-insoluble salt of a sulphonated oil in a fine state of dispersion throughout the composition.

3. A decorative coated sheet material including a base and a coating on the surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a water-soluble compound of a metal other than the metals of the first group of the periodic system and a sulphonated oil in a fine state of dispersion throughout the composition.

4. A decorative coated sheet material including a base and a coating on the surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a substance taken from the group comprising strontium hydroxide, barium hydroxide, calcium hydroxide and a sulphonated oil in a fine state of dispersion throughout the composition.

5. A decorative coated sheet material including a base and a coating on the surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and the products of the reaction between calcium hydroxide and a sulphonated oil in a fine state of dispersion throughout the composition.

6. A decorative coated sheet material including a base and a coating on the surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and the products of the reaction between calcium hydroxide and sulphonated castor oil in a fine state of dispersion throughout the film forming composition.

7. A decorative coated sheet material including a base and a coating on the surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a water-soluble salt of a metal other than a metal of the first group of the periodic system and a sulphonated oil in a fine state of dispersion throughout the film forming composition.

8. A decorative coated sheet material including a base and a coating on a surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a water-soluble salt of a metal other than a metal of the first group of the periodic system and a sodium neutralized sulphonated oil in a fine state of dispersion throughout the film forming composition.

9. A decorative coated sheet material including a base and a coating on a surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a water-soluble calcium salt and a sodium neutralized sulphonated castor oil in a fine state of dispersion throughout the film forming composition.

10. A coated sheet material including a moisture-pervious base impregnated with a size adapted to render the base substantially impervious to moisture and comprising a mixture containing a water-insoluble soap and a wax, and a decorated coating on a surface of the base in the form of a smooth, continuous, surface-hardened, flexible film having a highly polished surface and containing a film forming composition and a water-insoluble compound in a fine state of dispersion throughout the composition.

11. A coated sheet material including a moisture-pervious base impregnated with a size adapted to render the base substantially impervious to moisture and comprising a mixture containing a water-insoluble soap, a wax and a fatty acid, and a decorative coating on a surface of the base in the form of a smooth, continuous, surface hardened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a water-soluble compound of a metal other than the metals of the first group of the periodic system, and a sulphonated oil in a fine state of dispersion throughout the composition.

12. A coated sheet material including a moisture-pervious base impregnated with a size adapted to render the base substantially impervious to moisture and comprising a mixture containing aluminum oleate, paraffin and oleic acid, and a decorative coating on a surface of the base in the form of a smooth, continuous, surface-hard-

ened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a calcium salt and a sulphonated castor oil in a fine state of dispersion throughout the film forming composition.

13. The method of coating a moisture-pervious sheet which includes tub-sizing the sheet with a solution of a water insoluble size in an organic solvent, drying the sheet, and applying a film forming emulsion to a surface of the sized sheet.

14. The method of coating a moisture-pervious sheet which includes tub-sizing the sheet with a solution of a water insoluble size in an organic solvent, drying the sheet, applying a film forming emulsion to a surface of the sized sheet, drying the film formed on the surface of the sheet, and polishing the film.

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CERTIFICATE OF CORRECTION.

Patent No. 2,069,786. February 9, 1937.

PETER A. van der MEULEN.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 49, strike out the word "of"; line 51, for moisture, a coating composition which" read admixture therewith a water-insoluble; page 4, second column, line 49, claim 10, for "decorated" read decorative; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of March, A. D. 1937.

Henry Van Arsdale
Acting Commissioner of Patents.

(Seal)

ened, flexible film having a highly polished surface and containing a film forming composition and the reaction products of a calcium salt and a sulphonated castor oil in a fine state of dispersion throughout the film forming composition.

13. The method of coating a moisture-pervious sheet which includes tub-sizing the sheet with a solution of a water insoluble size in an organic solvent, drying the sheet, and applying a film forming emulsion to a surface of the sized sheet.

14. The method of coating a moisture-pervious sheet which includes tub-sizing the sheet with a solution of a water insoluble size in an organic solvent, drying the sheet, applying a film forming emulsion to a surface of the sized sheet, drying the film formed on the surface of the sheet, and polishing the film.

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