

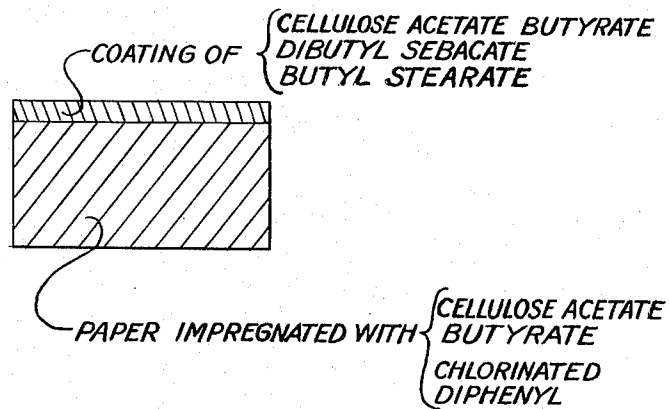
April 21, 1953

M. SALO ET AL

2,635,970

TRANSLUCENT PAPER BASE

Filed Nov. 26, 1948



Martin Salo
Harold F. Vivian

INVENTORS

BY *Daniel J. Mayne*
Newton M. Perrine
ATTORNEYS

UNITED STATES PATENT OFFICE

2,635,970

TRANSLUCENT PAPER BASE

Martin Salo and Harold F. Vivian, Rochester,
N. Y., assignors to Eastman Kodak Company,
Rochester, N. Y., a corporation of New Jersey

Application November 26, 1948, Serial No. 62,245

2 Claims. (Cl. 117—86)

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This invention relates to waterproof translucent paper prepared by impregnating paper with a low viscosity melt composition, followed by overcoating the impregnated paper in a melt-coating operation.

Waterproof translucent paper is useful for various purposes in the photographic art, particularly as a base for photographic copying and negative papers. Heretofore translucent paper has been prepared by applying a waterproof surface coating, such as from a volatile solvent solution of a cellulose ester, onto paper which by nature is translucent, such as glassine or parchment type paper. The operation of this method of preparing waterproof translucent paper from glassine has been difficult because of the low mechanical strength and poor dimensional stability of glassine paper.

One object of our invention is to provide a method of preparing translucent paper in which good tensile strength and good dimensional stability are found. Another object of our invention is to prepare a translucent paper which exhibits uniform properties both upon its preparation and after keeping for a long period of time. A further object of our invention is to provide translucent papers which are entirely free of discoloration, either upon preparation or in storage. A still further object of our invention is to provide a method for preparing translucent paper in which the use of solvents is unnecessary. Further objects of our invention will be apparent herein.

We have found that a translucent paper base is formed by first impregnating porous cellulose paper sheet with a melt composition and subsequently applying to the outside surface thereof a melt coating of good properties. The paper so prepared may be coated with a photosensitive emulsion and employed for photographic purposes.

The drawing accompanying this application illustrates a paper in accordance with one embodiment of our invention. The water-translucent paper there consists of a paper which has been impregnated with a composition of cellulose acetate butyrate and chlorinated diphenyl, which paper has a coating thereover of cellulose acetate butyrate plasticized with a mixture of dibutyl sebacate and butyl stearate. The paper thus illustrated is then ready for the application of a photosensitive emulsion thereover, such as a photosensitive gelatin-silver halide emulsion.

The paper which is employed is one substantially free from fillers (not more than 1%). The

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paper useful in our invention may be made from woodpulp, such as sulfate pulp or high α -cellulose sulfite pulp, rags, cotton, linen, hemp, or rope. Waterleaf paper, such as made from a free-draining pulp, is particularly good for use as the starting material in preparing translucent paper base in accordance with our invention. It is desirable that the paper have a high porosity as shown by its resistance to air being no higher than 15 seconds per 100 cc. of air at 70° F. and 50% relative humidity determined by the method of testing prescribed in TAPPI tentative standard T460M46.

The impregnating composition should have a low viscosity. This composition is applied as a melt to the paper and then subjected to treatment with pressure rolls or other pressing means exerting a pressure of at least 500 pounds per square inch at an elevated temperature. The paper should be one which has been prepared from a pulp which has not been beaten or hydrated to any great extent.

The impregnating composition to be employed should be a composition which forms a melt having a viscosity of less than 5000 centipoises at 170° C. It should be capable of melting at 300–330° F. and is usually composed of cellulose acetate butyrate having a butyryl content of at least 24% and diluting material therein, preferably a resin and a solvent type plasticizer. In some cases the cellulose ester can be omitted. In other cases the plasticizer may be omitted provided the resin employed has a softening effect on the cellulose ester. The impregnating composition is applied in the form of a melt at a temperature of 300–330° F. to the paper and subjected to a pressure of at least 500 pounds per square inch, such as by calendering rolls having a temperature of 300–330° F. The pressure and temperature should be less than that which will cause breaking or rupturing of the paper. Some of the impregnating compositions which are suitable for use in accordance with our invention are as follows:

- 60:35 polystyrene having a degree of polymerization of approximately 60 and butyl stearate
- 50:45:5 chlorinated diphenyl, cellulose acetate butyrate and dioctyl phthalate
- 75:25 chlorinated diphenyl having a chlorine content of 65% and cellulose acetate butyrate having a butyryl content of 50%
- 70:30:5 chlorinated diphenyl having a 60% chlorine content, cellulose acetate butyrate and dioctyl phthalate

The impregnating composition should contain a resin which imparts adhesiveness to the composition but is yet stable insofar that the resin is compatible with the other ingredients of the composition and is not guilty of blocking when applied as a melt coat. We have found that with cellulose acetate butyrate the chlorinated diphenyls having a chlorine content more than 40% are especially useful as the resin constituent. The cellulose ester employed must be a butyric acid ester of cellulose having a butyryl content of at least 42%.

The plasticizer employed in the impregnating composition should be a solvent-type plasticizer, such as dioctyl phthalate, dicapryl phthalate, dibutyl sebacate, di-ethyl-hexyl adipate, methoxyethyl phthalate, ethoxyethyl phthalate, and the like. These plasticizers can be mixed to a small extent with other types of plasticizers providing the resulting material remains of the solvent type or, in other words, will dissolve the cellulose ester at a temperature of 170–180° C. The impregnating composition in addition to having a viscosity below 5000 centipoises at 170° C. must also be a material which exhibits a refractive index close to that of the paper which is treated.

The overcoating composition which is applied as the second coat may be any melt-coating composition, such as described in patents relating thereto. This composition should be one which has a blocking point at about 200° F. and forms a coating which has satisfactory flexibility. A composition of 75 parts of a cellulose acetate butyrate having a butyryl content of 45%, 15 parts of dibutyl sebacate, and 10 parts stearate is useful for this purpose. Various melt-coating compositions which are eminently suitable for this overcoating have been described, such as in Salo Patents Nos. 2,387,773 and 2,387,774. Salo Patent No. 2,439,103 and Meyer Patent No. 2,439,093 also discloses melt-coating compositions useful as the overcoating referred to. Any of these compositions would be useful for the molten overcoating in preparing translucent paper base as described herein. Other melt-coating compositions, which are useful for overcoating purposes in accordance with our invention are described in British Patent No. 540,765, dated October 29, 1941.

The paper in accordance with our invention may be readily prepared by preheating the paper sheet to a temperature of 200–250° F. and then applying thereto in a melt-coating operation, such as described in British Patent No. 540,765, a melt of the impregnating composition held at a temperature of 300–330° F. The paper is then subjected to pressure, such as by calendering rolls having a temperature of 300–360° F. at a pressure exceeding 500 p. s. i. and preferably 3000 to 5000 p. s. i. A useful composition in this connection is made up of 50–70% of a chlorinated diaryl, particularly chlorinated diphenyl, having a chlorine content of at least 40%, 20–30% of a cellulose acetate butyrate having a low viscosity and a butyryl content of at least 45% and 5–15% of a solvent-type plasticizer. Compositions of this nature are described and claimed in U. S. Patent No. 2,481,687. Any of the compositions therein which have a chlorinated diphenyl or Aroclor content of at least 50% and a melting point of less than 200° C. would be useful for this impregnating operation.

After the impregnated paper has been obtained and the impregnating composition is set, the paper is then given an overcoating by passing the paper through a melt-coating machine in which

the paper is preheated to 300–330° F. and an overcoating composition at a temperature of 340–360° F. is applied thereto. Any of the melt-coating compositions referred to in my patents listed above or in British Patent No. 540,765, are useful in this operation, particularly to obtain a coating characterized by good flexibility. The clearance on the rolls employed in the coating operation should be such as to give a coat of .0003 to .0005 inch thickness on each side of the paper sheet. This aggregates 3 pounds of coating per side or 6 pounds of coating for both sides per 1000 square feet of paper surface. The product which is obtained readily transmits a large proportion of light and is useful for preparing translucent photographic papers.

It is desirable in applying an emulsion to this paper that subbing first be applied. One type of subbing which has been found to be useful in this connection is formed by first applying a very thin layer of a cellulose nitrate of quite low viscosity to the melt coating, followed by a very thin layer of gelatin applied thereto. The technique of subbing in this manner is described in U. S. Patent No. 2,014,547 of Babcock, granted September 17, 1935. The disclosure of that patent may be referred to as a guide for this type of subbing operation. If desired, instead of using two layers, the nitrate and gelatin may be mixed and applied as one layer. Instead of a nitrate layer, one may employ a layer of a mixed cellulose ester, such as hydrolyzed cellulose acetate propionate or butyrate. As a matter of fact, any of the usual types of subbing layers which have been described in the prior art and which are compatible with the photographic emulsion layer to be employed and the melt-coating surface may be used if a subbing layer should be thought to be necessary. The sensitized emulsion which is employed may be any of the usual gelatin silver-halide emulsions. In some cases it may be desirable to employ an emulsion in which a cellulose ester is employed as the protective colloid, such as described and claimed in U. S. Patent 2,110,491 of Salo.

The following examples illustrate our invention:

Example 1.—Porous waterleaf paper was impregnated by means of hot calendering rolls on a Waldron type melt-coating machine after first heating the paper to 200–250° F. and coating it with a melt at 320° F., consisting of 35% of cellulose acetate butyrate having a 50% butyryl content and 25 cps. viscosity, 60% of chlorinated diphenyl having a chlorine content of 65% and 5% of dioctyl phthalate. After thus impregnating the paper it was found to transmit a considerable amount of light or, in other words, exhibit a good degree of translucency. The translucent impregnated paper was then overcoated on the melt-coating machine on both sides by heating the paper to 300–330° F. and then applying at a temperature of 350° F. a melt consisting of 75 parts of cellulose acetate butyrate of 50% butyryl and 25 cps. viscosity, 15 parts of dibutyl sebacate, and 10 parts of butyl stearate. The coating rolls were set so as to give a thickness on each side of approximately .0005 inch, the melt having been applied at the rate of six pounds per 1000 square feet of surface. The coated product which had a light transmission of about 60% was subbed by applying a thin layer of cellulose nitrate of low viscosity and then a thin layer of gelatin thereto. The paper was then coated with a photosensitive gelatin-silver halide emulsion, and the result-

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ing product was found to be satisfactory as a photographic copying and negative paper. Also, the product obtained was found to store satisfactorily.

Example 2.—Porous waterleaf paper was impregnated as described in the preceding example with a mixture of 45 parts of low viscosity cellulose acetate butyrate having a butyryl content of 50%, 50 parts of chlorinated diphenyl dioctyl phthalate. The impregnated paper was then overcoated as described in the preceding example. The paper thus obtained was subbed and then coated with a photosensitive gelatin silver halide emulsion. A translucent photographic paper having good properties was obtained.

Example 3.—Porous waterleaf paper was impregnated as described in Example 1 with a composition of 75 parts of chlorinated diphenyl having a chlorine content of 65% and 25 parts of cellulose acetate butyrate having a butyryl content of 50% and a viscosity of 10 centipoises. The impregnated paper obtained was then overcoated as described in Example 1. A translucent photographic paper base was obtained having good light transmission.

Example 4.—Porous waterleaf paper was impregnated as described in Example 1 using a composition of 60 parts of polystyrene having a degree of polymerization of about 60 and 35 parts of butyl stearate. The thus-impregnated paper was overcoated with a melt composition as described in the preceding examples. A translucent photographic paper base having good properties was obtained.

When viscosities of cellulose acetate butyrates are referred to in the above examples, they are expressed in the viscosity of a solution of one part of the ester in nine parts of acetone at 25° C. The low viscosity butyric acid esters of cellulose which are employed in the melt-coating operation in preparing photographic paper in accordance with our invention are those which have a melting point of less than 200° C., a char point of at least 260° C., and preferably at least 300° C., a fundamental cuprammonium viscosity of not more than 10 centipoises, and an acetone viscosity within the range of 5-100 centipoises. The cellulose ester should have a butyryl content of at least 42% and should be hydrolyzed little, if any. For instance, a hydroxyl content of less than 1 hydroxyl per 4 glucose units is typical of the hydroxyl content of cellulose esters which are suitable. Some cellulose esters having the properties stated and suitable for melt coating in accordance with our invention are:

1. Cellulose acetate butyrate, butyryl content 47.7%, acetyl content 6.5%, acetone viscosity 24.9 centipoises.

2. Cellulose acetate butyrate, butyryl content 49.4%, acetyl content 5.6%, acetone viscosity 20 centipoises.

3. Cellulose acetate butyrate, butyryl content 48%, acetyl content 6.2%, acetone viscosity 15 centipoises.

4. Cellulose acetate butyrate, butyryl content 52%, acetyl content 1.5%, acetone viscosity 22 centipoises.

5. Cellulose butyrate, butyryl content 55%, acetone viscosity 16 centipoises.

In the translucent paper base in accordance with our invention, the best products have been

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obtained in cases where the impregnating composition has constituted amounts within the range of 20-45% of the total. Some papers which have been found to be of excellent character, the impregnating composition having a refractive index approximately that of the paper sheet, are as follows:

	Paper		Impregnant		Overcoating	
	Wt. (lbs.) per 1,000 sq. feet	Per- cent	Wt. (lbs.) per 1,000 sq. feet	Per- cent	Wt. (lbs.) per 1,000 sq. feet	Per- cent
waterleaf.....	12	40	8.9	30	8.8	30
Do.....	12	45	9.0	33	5.8	22
hemp paper....	6.1	36	4.8	28	6.1	36

The preparation of translucent paper base in accordance with our invention admits of continuous operation in that paper sheet comes in the form of rolls, the usual melt coating machines are adapted for continuous operation, and the temperatures used for impregnating the paper correspond fairly closely to those to which it is desirable to preheat the paper in the melt coating operation which constitutes the second step of our process. We have found that by preparing translucent paper base in this manner, the process becomes a unitary operation, the paper going in at one end, being coated with the impregnant, hot calendered, melt coated again to apply the overcoating thereto and coming out as a finished product which after having cooled below the melting point of the overcoating, may be collected on rolls.

We claim:

1. A water-proof translucent paper consisting of paper having a loose porous structure impregnated with a composition solid at room temperature consisting of cellulose acetate butyrate and chlorinated diphenyl, the latter constituting at least 50% of the composition, which composition has a viscosity of less than 5000 centipoises at 170° C. and a refractive index approximately that of paper and having as an overcoat thereon a coating essentially consisting of cellulose acetate butyrate, dibutyl sebacate and butyl stearate.

2. A water-proof translucent paper consisting of paper having a loose, porous structure impregnated with a composition solid at room temperature consisting of approximately 25 parts of cellulose acetate butyrate and approximately 75 parts chlorinated diphenyl which composition has a viscosity of less than 5000 centipoises at 170° C. and a refractive index approximately that of paper and having as an overcoat thereon a coating essentially consisting of cellulose acetate butyrate dibutyl sebacate and butyl stearate.

MARTIN SALO.
HAROLD F. VIVIAN.

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