

PATENT SPECIFICATION

1,012,120

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Date of Application and filing Complete

Specification: November 14, 1961.

No. 40720161

Complete Specification Published: December 8, 1965.

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Index at Acceptance:—D2 B (12, 14A, 14H, 14X); B6 C (A12, A25).

Int. Cl.:—D 21 h // B41f.

COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in or relating to the Treatment of Paper and Paper Products

WE, CUSTOMARK CORPORATION, a corporation organised and existing under the laws of the State of Wisconsin, United States of America, of 405 South Appleton Street, Appleton, Wisconsin, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

This invention relates to the treatment of paper and paper products.

In commercial enterprises it is often desirable to provide a watermark on stationery and other business and professional papers. For example, business trade marks are often watermarked for identity and protective purposes, and such watermarking serves as an additional means of associating the mark with a particular business enterprise.

The present practice of watermarking is generally performed during the paper-making process by providing embossed rolls interposed usually at a point before the wet paper web enters the dryers. The fibres in the web are thereby displaced in a horizontal direction, and the paper is thus rendered thinner and consequently more transparent at the area of the watermark by the embossed rolls which form the mark in the damp or wet paper. After the paper making and watermarking process is complete, the finished paper is cut into sheets of the desired size.

Another method of forming a watermark involves the use of a band fitted about a roll and carrying the design of the watermark in relief. The design is brought into contact with the wet paper web at the wet presses beyond the fourdrinier or wet end. At that point the paper is still plastic and compresses readily. The resulting com-

pression of fibres, reducing entrapped air and light refraction, increases the transparency of the area of the watermark.

Watermarked paper made by the methods described above has several disadvantages. Firstly, the commercial paper making machines are very large and produce paper at a high volume rate. Thus, for economic reasons, a customer desiring stationery bearing a private watermark such as a trade mark must purchase a large amount of each kind of paper needed. This of course limits the use of privately-watermarked papers to a few relatively large industrial users or government departments.

Secondly, the cost of the embossed or banded rolls for the paper making machine is very high and cannot therefore be afforded by smaller industrial users. Thirdly, the cost of setting up the embossed or banded rolls involves labour cost as well as loss of production on the paper making machinery which must all be taken into account in the net cost to the purchaser. Furthermore, among other disadvantages, the private watermark is not positioned uniformly in the finished cut stationery unless he assumes the additional labour cost and paper waste involved in constantly positioning the rolled paper and cut-off knife. Thus, while private watermarks may be formed by these methods, it is clear that orders for paper products so marked must be large if the cost is to be justified.

One of the aims of the present invention is to overcome the above-mentioned disadvantages.

The general principle underlying the invention, in so far that it relates to the formation of watermarks in paper, is that blank paper (i.e. paper having no watermark) is so impregnated with a novel chemical composition that, after drying,

[Price 4s. 6d.]

Price 25p

transparent areas are created in the paper sheet conforming to the desired configuration of the watermark. The resulting watermark possesses for all practical purposes the same general characteristics in use as that of a watermark formed by the earlier processes described above.

A chemical composition suitable for forming a watermark in the manner mentioned above must have the ability to mark the paper in such a way as to render it more translucent or substantially transparent in the impregnated area. Further, the chemical composition should not alter the surface of the paper adversely. For example, it must not render the surface glossy in the impregnated area and must not alter the erasability characteristic of the paper. In addition, the chemical composition must withstand aging without discoloration and must not become indistinct through migration of the chemical or otherwise. And of course, quite apart from low cost, the watermarked area must accept typing, pencilling, printing and writing inks without adverse effects such as feathering or skipping.

A watermark, from a fundamental viewpoint, possesses a translucency of higher degree of transparency in the marked area than that possessed by the paper in the unmarked areas. The most common type of watermark appears more transparent than the surrounding unmarked paper.

After considerable experimental work, we have found that certain organic compounds, when properly applied to or impregnated into the paper, impart to the paper sheet a watermark which is more translucent than the surrounding paper. Chief among these organic compounds are the following:

1. Sodium dodecyl sulfosuccinate
2. Sucrose acetate isobutyrate
3. Sodium dihexyl sulfosuccinate
4. Sodium diamyl sulfosuccinate

Although sodium dioctyl sulfosuccinate, sodium dihexyl sulfosuccinate and sodium diamyl sulfosuccinate have been found to be excellent for the purpose of this invention, corresponding salts of other alkali metals are equally applicable for the same purpose. Likewise, in the case of sucrose acetate isobutyrate, the isobutyrate radical may well be substituted with a normal butyrate radical, the chemical and physical analogy between these two radicals being substantially the same. Furthermore, it appears that none of these organic chemicals enter into chemical reaction with the constituents of the paper. Rather it appears to be a matter of obtaining proper displacement of entrained air with these organic compounds to create a satisfactory mark in the paper.

In order to obtain the necessary degree

of impregnation or coating with the above described organic compounds, certain fundamental characteristics of the paper sheet must be considered. For example, the thickness, composition and weight (i.e. density) of the paper sheet are variables and must be considered. Surprisingly, however, it has been found that such variables are largely overcome by adjusting the concentration of the above described chemicals in selected organic solvents. The selection of the organic solvent as a carrier is important, for if the solvent evaporates at an excessive rate the penetration of the paper is insufficient to result in proper impregnation by the organic solutes employed. On the other hand, if the solvent evaporates too slowly, the organic solutes tend to migrate in the paper resulting in an indistinct watermark. In this respect it has been found that inert organic solvents having boiling points at atmospheric pressure in the range of 100°C. to 250°C. possessed vapour pressures at room temperatures suitable for this invention. The term "inert" as used herein is intended to mean that the solvent does not enter into any chemical reaction under the conditions of this invention.

Stated in its broadest terms, the method of the invention comprises applying to paper or a paper product a liquid solution containing 30% to 70% by weight of sucrose acetate butyrate or isobutyrate and/or an alkali metal salt of an alkyl sulfosuccinate, the balance of 70% to 30% by weight comprising an inert organic solvent therefor having a boiling point in the range of 100°C. to 250°C. Concentrations of the compounds in solvents above 70% by weight are found to produce indistinct watermarks due to insufficient penetration of the paper, while concentrations below 30% by weight produce watermarks of insufficient visibility in reflected or transmitted light.

Some of the solvents successfully employed in compositions according to this invention include ethylene glycol, diethylene glycol monoethyl ether (Carbitol), ethylene glycol monoethyl ether, ethylene glycol diethyl ether, benzyl alcohol, 2-(2-methoxyethoxy)-ethanol, ethylene glycol monophenyl ether and ethylene glycol monoethyl ether.

In order to evaluate the various compositions in this invention, watermarks of excellent quality were obtained in the laboratory by hand impregnation. The hand impregnation was accomplished by depositing a small metered amount of the composition on the surface of a foot-square piece of one-quarter inch thick plate glass. The composition was spread uniformly over the glass surface with the aid of an engraved roll bearing 75 depressions per inch and fitted with a handle. A die or hand stamp of rubber-like material having inscribed on 130

the face thereof a typical watermark design was first pressed against the wet film of the composition on the glass and then stamped on the paper sheet. The watermark-
5 marked paper sheet was allowed to dry and then examined.

By way of illustration, excellent watermarks were obtained by laboratory hand impregnation, as described above, using the
10 compositions listed below. In each case the stated proportions are in terms of weight:

<i>EXAMPLE I</i>		
	Sodium dioctyl sulfosuccinate	50%
	2-methoxy-ethanol	50%
15	<i>EXAMPLE II</i>	
	Sodium dioctyl sulfosuccinate	50%
	2-methoxy-ethanol	25%
	<i>EXAMPLE III</i>	
	Sodium dioctyl sulfosuccinate	50%
20	Diethylene glycol monoethyl ether	50%
	<i>EXAMPLE IV</i>	
	Sucrose acetate isobutyrate	50%
	Ethylene glycol monomethyl ether	50%
	<i>EXAMPLE V</i>	
25	Sucrose acetate isobutyrate	50%
	Diethylene glycol monoethyl ether	50%
	<i>EXAMPLE VI</i>	
	Sucrose acetate isobutyrate	35%
	Diethylene glycol monoethyl ether	65%
30	<i>EXAMPLE VII</i>	
	Sucrose acetate isobutyrate	50%
	Ethylene glycol monoethyl ether	50%
	<i>EXAMPLE VIII</i>	
	Sodium dioctyl sulfosuccinate	50%
35	Diethylene glycol monoethyl ether	50%
	<i>EXAMPLE IX</i>	
	Sodium dioctyl sulfosuccinate	40%
	Sucrose acetate isobutyrate	10%
	Diethylene glycol monoethyl ether	50%
40	<i>EXAMPLE X</i>	
	Sodium dioctyl sulfosuccinate	25%
	Sucrose acetate isobutyrate	25%
	Diethylene glycol monoethyl ether	50%
	<i>EXAMPLE XI</i>	
45	Sodium dioctyl sulfosuccinate	10%
	Sucrose acetate isobutyrate	40%
	Diethylene glycol monoethyl ether	50%
	<i>EXAMPLE XII</i>	
	Sodium dihexyl sulfosuccinate	50%
50	Diethylene glycol monoethyl ether	50%
	<i>EXAMPLE XIII</i>	
	Sodium diamyl sulfosuccinate	50%
	Benzyl alcohol	50%
	<i>EXAMPLE XIV</i>	
55	Sodium diamyl sulfosuccinate	50%
	2-(2-methoxyethoxy) ethanol	50%
	<i>EXAMPLE XV</i>	
	Sodium dioctyl sulfosuccinate	0.05%
	Sucrose acetate isobutyrate	49.95%
60	Diethylene glycol monoethyl ether	50.00%
	<i>EXAMPLE XVI</i>	
	Sodium dioctyl sulfosuccinate	0.25%
	Sucrose acetate isobutyrate	49.75%
65	Diethylene glycol monoethyl ether	50.00%

ether	50.00%	
<i>EXAMPLE XVII</i>		
Sodium dioctyl sulfosuccinate	0.5%	
Sucrose acetate isobutyrate	49.5%	
Diethylene glycol monoethyl ether	50.0%	70
<i>EXAMPLE XVIII</i>		
Sodium dioctyl sulfosuccinate	1.0%	
Sucrose acetate isobutyrate	49.0%	
Diethylene glycol monoethyl ether	50.0%	75
<i>EXAMPLE XIX</i>		
Sodium dihexyl sulfosuccinate	2.5%	
Sucrose acetate isobutyrate	47.5%	
Diethylene glycol monoethyl ether	50.0%	80

Accelerated aging of the watermarks in the above examples at 150°F. for 72 hours showed no discolouration.

In the above examples the blank paper product employed was of bond grade consisting of 25% cotton and 75% chemical woodpulp, its thickness being about 4.0
85 mils. The resulting watermarks possessed a high degree of transparency.

In the paper industry the terms "opaque" and "semi-opaque" can refer to varying levels of opacity, depending on the specific type of paper under discussion. For purposes herein, more definite meanings can be given these terms by the following explanation.
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In the field of writing paper, trade practice classifies an "opaque" sheet of bond paper as one of a standard weight (500 sheets, cut 17 inches by 22 inches, weighing between 19.5 lbs. and 20.5 lbs.) having a TAPPI opacity in excess of 87%, this percentage being the reciprocal of the percentage of monochromatic light which is able to pass through the paper and be photometrically measured.
100

The less commonly used term, "semi-opaque," is generally accepted by the trade as a standard weight sheet of bond paper having a TAPPI opacity somewhere between 87% and 65%.
110

Writing papers having a TAPPI opacity less than 65% are often referred to as "transparent." It will suffice to say that, the lower the TAPPI opacity, the more often the trade refers to "transparency," and the closer the opacity is to 65%, the more often the trade uses the term "translucent." Translucent papers usually retain the more common characteristics of bond papers, such as formation and brightness, whereas transparent sheets most often have more uniformly translucent fibre mass with considerably less brightness.
125

This explanation holds true whether the paper under discussion is made entirely of chemical wood pulp, a blend of chemical wood pulp and cotton or linen fibres, or entirely of cotton and/or linen fibres.
130

Technically, the term "translucent" usually implies that a ray of light passing through a material is diffused, while the term "transparent" implies that a ray of light passing through is not diffused. Thus, a translucent object may vary from opaque to true transparency according to the magnitude of diffusion of light passing therethrough. However, for purpose of this discussion the term transparency is used to denote that the magnitude of diffusion of light passing through the paper is not greater than that found in commercial tracing paper. If, therefore, a sheet of paper possesses a TAPPI opacity less than 65%, it is termed herein as "transparent" and conversely if 65% or greater it is termed herein as "translucent."

In the foregoing examples the areas covered by the watermark on paper known commercially as "opaque" and "semi-opaque" were distinct and transparent. In the same manner the entire translucent blank paper known commercially as "opaque" and "semi-opaque" may be converted from a translucent paper to a transparent paper. Several successful tests were made in the transparentizing of entire sheets of translucent paper of the type used in the above examples employing the same compositions. The transparency of the products obtained was greater than that of some commercial tracing papers.

At this point it should be mentioned that in the transparentizing of a sheet of paper, the matter of migration of the chemical impregnant over a period of time becomes unimportant as distinguished from the process of forming watermarks. Migration of the chemical impregnant in the case of watermarks may necessarily not occur as such migration would tend to obliterate the mark over a period of time.

Transparentized paper has many commercial uses such as tracing paper and the like. Also, there is a commercial demand for translucent paper having only a portion of the sheet transparentized such as the window type mailing envelopes wherein the address is printed on the contents of the envelope and positioned beneath the transparent window.

In order to confirm the laboratory hand impregnating technique employed in the above examples, the novel compositions of this invention were employed in forming watermarks on blank paper by means of a commercially usable process. The results of the commercial type application of the invention are illustrated in the following additional examples, the proportions being in terms of weight.

EXAMPLE XX

Composition A
 65 Sucrose acetate isobutyrate 50%

Diethylene glycol monoethyl ether 50%

Paper

Bond grade, 25% cotton - 75% chemical wood pulp, having a thickness of 4.0 mils and an apparent density of 5.0 The rate of paper travel or production was 40 feet per minute. 70

The resulting watermark was clear and distinct.

EXAMPLE XXI

Composition B

Sucrose acetate isobutyrate 10%
 Sodium dioctyl sulfosuccinate 40%
 Diethylene glycol monoethyl ether 50%

Composition A

Sucrose acetate isobutyrate 50%
 Diethylene glycol monoethyl ether 50%

Paper—Same as in Example XX.

The watermark was first applied on one side employing composition B and then, in register, the other side employing composition A. The rate of application on each side was the same as that of Example XX. The resulting watermark was clear and distinct. 85 90

EXAMPLE XXII

Same as Example XXI except the following composition C was substituted for Composition B.

Composition C

Sucrose acetate isobutyrate 37.5%
 Sodium dioctyl sulfosuccinate 12.5%
 Diethylene glycol monoethyl ether 50.0%

The resulting watermark was clear and distinct. 95 100

EXAMPLE XXIII

Same as for Example XXI except that the paper employed had additional sizing. The resulting watermark was clear and distinct. 105

EXAMPLE XXIV

Same as Example XXIII except that the rate of application was increased to 100 feet per minute. The resulting watermark was distinct. 110

EXAMPLE XXV

Same as Example XXII except that onion-skin paper was employed. The resulting watermark was clear and distinct. 115

EXAMPLE XXVI

Same as Example XXII except that onion-skin paper was employed and treated only on one side using composition C. The resulting watermark was clear and distinct. 120

EXAMPLE XXVII

Same as Example XXII except that onion-skin paper was employed and treated only on one side using Composition A. The resulting watermark was clear and distinct. 125

Satisfactory results were also achieved in the commercial type application of the invention in the following examples in which a clear and distinct watermark was achieved:

130

EXAMPLE XXVIII

	Sodium dioctyl sulfosuccinate	1.6%
	Sucrose acetate isobutyrate	48.4%
5	Diethylene glycol monoethyl ether	50.0%

EXAMPLE XXIX

	Sodium dioctyl sulfosuccinate	20%
	Sucrose acetate isobutyrate	30%
10	Diethylene glycol monoethyl ether	50%

EXAMPLE XXX

	Sodium dioctyl sulfosuccinate	30%
	Sucrose acetate isobutyrate	20%
10	Diethylene glycol monoethyl ether	50%

EXAMPLE XXXI

15	Sodium dioctyl sulfosuccinate	37.8%
	Sucrose acetate isobutyrate	12.2%
	Diethylene glycol monoethyl ether	50.0%

Generally, it was found unnecessary to apply the watermark on both sides, but in some instances application of the watermark on both sides, in register, was advantageous, particularly on thick and dense papers. Forced drying, such as by radiant heat, generally was found to be unnecessary. However, where the design of the watermark is characterised by large areas it may be advantageous to force-dry the sheets to prevent migration of the chemical which may occur if drying is too slow.

It has thus been shown that ordinary grades of writing stationery can be provided with a watermark by chemical impregnation according to this invention by means of hand impregnating or commercially acceptable application methods. From this it can be readily appreciated that small quantities of paper may be provided with such marking at costs which meet the requirements of smaller volume customers and thereby making available, economically, a long sought paper product. Further, the invention enables manufacturers to transparentize economically translucent paper products, such as that commercially known as "opaque" and "semi-opaque" papers, in order to produce tracing papers and the like.

The amount of impregnating composition used may vary due to the type and density of the paper being treated. An amount sufficient to reduce the TAPPI opacity to

below 65% is necessary in order to transparentize translucent paper. In the case of the bond paper used in the examples, an amount of impregnating composition which represented 15% of the weight of the paper gave satisfactory results.

WHAT WE CLAIM IS:—

1. A method of treating paper or a paper product so as to produce a watermark in it or to increase its transparency, which method comprises applying to the paper a liquid solution containing 30% to 70% by weight of sucrose acetate butyrate or isobutyrate and/or an alkali metal salt of an alkyl sulfosuccinate, the balance of 70% to 30% by weight comprising an inert organic solvent therefor having a boiling point in the range of 100°C. to 250°C.

2. A method according to claim 1, in which the liquid solution comprises an alkali metal salt of dioctyl sulfosuccinate, dihexyl sulfosuccinate, or diamyl sulfosuccinate.

3. A method according to claim 2, in which the alkali metal is sodium.

4. A method according to any preceding claim, in which the solvent comprises diethylene glycol monoethyl ether, ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol diethyl ether, 2-(2-methoxy ethoxy) ethanol, ethylene glycol monoethyl ether, or benzyl alcohol.

5. A method according to claim 1, in which the liquid solution comprises from 0.3% to 40% by weight of sodium dioctyl sulfosuccinate or sodium dihexyl sulfosuccinate, and from 10% to 69% by weight of acetate isobutyrate.

6. A method of treating paper or a paper product so as to produce a watermark in it or to increase its transparency, which method comprises applying to the paper a liquid solution of the composition given in any one of Examples I to XXXI set forth herein.

7. Paper or a paper product treated by the method of any one of claims 1-6.

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EXAMPLE XXVIII

	Sodium dioctyl sulfosuccinate	1.6%
	Sucrose acetate isobutyrate	48.4%
5	Diethylene glycol monoethyl ether	50.0%

EXAMPLE XXIX

	Sodium dioctyl sulfosuccinate	20%
	Sucrose acetate isobutyrate	30%
10	Diethylene glycol monoethyl ether	50%

EXAMPLE XXX

	Sodium dioctyl sulfosuccinate	30%
	Sucrose acetate isobutyrate	20%
10	Diethylene glycol monoethyl ether	50%

EXAMPLE XXXI

15	Sodium dioctyl sulfosuccinate	37.8%
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	Diethylene glycol monoethyl ether	50.0%

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 20 apply the watermark on both sides, but in some instances application of the watermark on both sides, in register, was advantageous, particularly on thick and dense papers. Forced drying, such as by radiant heat,
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 30 may occur if drying is too slow.

It has thus been shown that ordinary grades of writing stationery can be provided with a watermark by chemical impregnation according to this invention by means of
 35 hand impregnating or commercially acceptable application methods. From this it can be readily appreciated that small quantities of paper may be provided with such marking at costs which meet the requirements of
 40 smaller volume customers and thereby making available, economically, a long sought paper product. Further, the invention enables manufacturers to transparentize economically translucent paper products,
 45 such as that commercially known as "opaque" and "semi-opaque" papers, in order to produce tracing papers and the like.

The amount of impregnating composition
 50 used may vary due to the type and density of the paper being treated. An amount sufficient to reduce the TAPPI opacity to

below 65% is necessary in order to transparentize translucent paper. In the case of the bond paper used in the examples, an
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WHAT WE CLAIM IS:—

1. A method of treating paper or a paper
 60 product so as to produce a watermark in it or to increase its transparency, which method comprises applying to the paper a liquid solution containing 30% to 70% by
 65 weight of sucrose acetate butyrate or isobutyrate and/or an alkali metal salt of an alkyl sulfosuccinate, the balance of 70% to 30% by weight comprising an inert organic solvent therefor having a boiling point in
 70 the range of 100°C. to 250°C.

2. A method according to claim 1, in which the liquid solution comprises an alkali metal salt of dioctyl sulfosuccinate, dihexyl sulfosuccinate, or diamyl sulfosuccinate.
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3. A method according to claim 2, in which the alkali metal is sodium.

4. A method according to any preceding claim, in which the solvent comprises diethylene glycol monoethyl ether, ethylene
 80 glycol, ethylene glycol monomethyl ether, ethylene glycol diethyl ether, 2-(2-methoxyethoxy) ethanol, ethylene glycol monoethyl ether, or benzyl alcohol.

5. A method according to claim 1, in
 85 which the liquid solution comprises from 0.3% to 40% by weight of sodium dioctyl sulfosuccinate or sodium dihexyl sulfosuccinate, and from 10% to 69% by weight of acetate isobutyrate.
 90

6. A method of treating paper or a paper product so as to produce a watermark in it or to increase its transparency, which method comprises applying to the paper a liquid solution of the composition given in
 95 any one of Examples I to XXXI set forth herein.

7. Paper or a paper product treated by the method of any one of claims 1-6.

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