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COMPLETE SPECIFICATION

Chemical Shadow Mark

We, CUSTOMARK CORPORATION, a corporation organised and existing under the laws of the State of Wisconsin, United States of America P.O. Box 678 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 a paper article having an area of increased opacity and to a method of chemically opacifying paper.

Shadow watermarks are those in which the density of the paper fibres in a portion of a sheet of paper is decreased relative to the remaining portions of the paper. Such shadow watermarks are conventionally formed in the papermaking process where a wet web of paper on a Fourdrinier is contacted with a dandyroll having an indented or recessed surface conforming to the design which will be formed on the paper. During such contact the paper fibres accumulate in the recessed or indented surface, and this results in decreased density of paper fibres in that localized area. Such shadow marks tends to be opaque marks which transmit less light relative to the remainder of the paper. The conventional watermark is formed by a reverse procedure in which a dandyroll with a raised design contacts the wet paper in spread the paper fibres and increase their density in that localized area. Such increased density results in the translucence of the typical well-known paper mark.

In United States Patent No: 3,085,898 and 3,140,959 paper articles and method are described wherein chemical translucent watermarks are formed by an economical procedure which obviates the expense and complexity of the conventional watermark formation. It is likewise desirable to obtain a paper article which has a simple and economically produced shadow watermark to obviate the complexity of the conventional watermark formation. It is likewise desirable to obtain a paper article which may be entirely opacified by a simple and economical process.

It is a primary aim of this invention to provide a paper article and a method whereby opaque areas can be imparted to finished sheets of paper.

Accordingly this invention provides a paper article having an area comprising a cured, thermosetting resin, the resin being absorbed into the paper and being raised at least 5% relative to the original thickness of the paper, and the area having an opacity which is increased at least 1% relative to the original light transmission of the paper.

This invention also provides a method of chemically opacifying paper, which comprises applying to the surface of the paper an area of a liquid composition containing a thermosetting curable resin, a curing agent therefore, and an organic solvent; contacting said area with water before said thermosetting resin has hardened; and curing said thermosetting resin on said paper until said thermosetting resin hardens.

In the method of the invention it is preferred that the hardened thermosetting resin is raised at least 5% relative to the original thickness of the paper, and the opacified paper has an opacity which is increased at least 1% relative to the original light transmission of the paper.

The opaque areas may be imparted either in a selected design or entirely throughout the article by a few manipulative steps in which the surface of a sheet of paper is variously treated to form thereon opaque areas that will be as serviceable as the original paper.

It is not necessary to take care that the water or aqueous sizing solution only contacts the design laid onto the surface of the paper.

If desired an opaque area can be obtained by initially applying a thermosetting resin and curing agent to cover the entire surface, and then contacting the entire paper surface with water or an aqueous sizing solution. When using the aqueous sizing agent, an opaque

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Price 25p

area is formed by a step which simultaneously sizes the paper and participates in forming the opaque area.

For convenience, the process leading to one form of the paper article may be summarized as follows:

(A) Impart liquid composition containing thermosetting resin curing agent therefore, and an organic solvent to surface of a finished sheet of paper

(B) Contact the resin and curing agent with water or an aqueous sizing solution before the resin cures into a hardened form

(C) Curing the thermosetting resin with the contacted water or an aqueous sizing solution to render the configuration less translucent than the balance of the paper

The above summarized process which may either be directed to opaqueing entire sheets, or a portion in a selected design to obtain a shadow mark known also as a shaded mark or watermark.

United States Patent No. 3,140,959, issued July 14th, 1964, teaches how to economically make a paper product with a chemical watermark by contacting the surface of the paper by means conforming to a selective design, said means having or being wetted with a liquid composition containing a thermosetting resin in an organic solvent. When such composition contacts the paper, that portion of the paper becomes more translucent than the balance of the paper, and such greater translucency is maintained after the thermosetting chemical watermark cures into a hardened form. Such a chemical watermark is firmly adhered to the paper, is ink receptive, and is not removable by ordinary solvents or mechanical eraser means.

The first step (A) above may use a similar liquid composition containing thermosetting resin and a curing agent as is disclosed in said United States Patent No. 3,140,959. Said resin and curing agent may be referred to as impregnating materials. The liquid composition includes organic solvent which, after removal by evaporation, would render the paper translucent in the area of the hard chemical watermark. The liquid composition may be applied to the surface of the sheet of paper by various means, for example by printing by or brushing the mark through a stencil. In any event, such an area is subsequently treated with the water or the aqueous sizing solution before the thermosetting resin in the liquid composition has hardened into what would be the chemically translucent area according to United States Patent No. 3,140,959. After the liquid composition containing the impregnating materials contacts a sheet of paper the solvent in the liquid composition immediately begins to evaporate off. It is preferred that the step of contacting the area containing the impregnating materia' with the water or sizing solution occurs pri to evaporation of all the solvent. In any even the important feature is that contact with th water or the sizing solution should occur before the thermosetting resin cures into a hardened film. Reference may be made to the resin as becoming hard or hardened, and such a term is intended to designate the state in which the resin is obtained following an adequate period of curing by an appropriate curing agent.

Various sizing solutions are commonly used, and the most popular are starch solutions, such as chlorinated and ethylated starches. Other sizing agents in water solutions include the animal, bone and hide glues.

Following step (B) above, the resin area has not yet attained an opaque state, or a condition in which area is less translucent than the area was in the original paper. Step (c) above requires that the resin area, contacted with water or the aqueous sizing solution, is cured into a hard form. The curing is preferably effected by heating and results in the resin area becoming opaque, wherein it is less translucent than the remaining portion of the paper. Although heating is the preferred method of cure, the heat curing is preferably not effected at a high temperature as this merely accelerates the rate of cure. If desired, a room temperature cure may be conducted although extended periods are required to cure the resin into a desirably hard form. The nature of the interaction between the thermosetting resin and the water or sizing solution is not known with certainty, but apparently some incompatibility occurs between the water, alone or in the sizing solution, and the thermosetting resin. Irrespective of the correct explanation, there is obtained a paper article having an opaque area which stands up under mechanical abrasion such as erasing, has excellent ink receptivity, and generally has a desirably useful period of life.

Thermosetting resins of the type disclosed in United States Patent No. 3,140,959 may be used in this process and they include a formaldehyde, a polyester and a phenol-formaldehyde resin, as well as their appropriate curing agents.

Particularly successful opaque areas have been obtained by employing an epoxy resin and an appropriate curing agent as the impregnating material in the liquid composition. The liquid composition may have various consistencies depending on the amounts of the thermosetting resin therein. It is necessary for the consistency of the composition to be such that it can be easily applied to the surface of a finished paper. In general, the amount of thermosetting resin may be about one-half of the liquid composition by weight. The amount of the thermosetting resin and the appropriate curing agent may be variously

modified, for example depending on the rate of cure desired or the degree of the hardness desired. By way of illustration, the liquid composition may be transferred to the paper by using a pick up roll to transfer the liquid composition onto a transfer roll and then onto a plate roll which may have an unbroken surface for covering an area equal to the entire sheet, or the surface may have a selected design formed on a material such as a rubber plate. The plate roll contacts the paper web which is against a backing roll and then the paper web, containing the translucent chemical area, is moved to be contacted with water or sizing solution.

The sizing solution may be a conventional chlorinated starch and water solution which has been cooked at a sufficient temperature to swell the starch granules into an operable solution. Various starch concentrations in water may be maintained at moderate temperatures ranging from about room temperature to about 150°F. Such a sizing solution may be in a conventional size tub and the paper web may be moved to such tub to complete the contact of paper and the starch solution. Various equivaleut means are known in the art for sizing paper. In addition to a size tub, there is, for example, a horizontal size press with puddles, and kiss coating. When referring to "sizing" herein, reference is intended to surface sizing rather than internal sizing. After the paper web has left the size tub, it may be nipped between rollers to remove excess starch. It is seen that in this step the entire web of paper is coated with a starch solution so that the paper is simultaneously sized and the translucent impregnating compound contacted with the starch sizing solution. This is an advantage of the process because paper can then be conventionally sized while, at the same time, opacifying the sheet or forming a shadow chemical watermark.

The web of paper which has been contacted with the sizing solution has a resin impregnated area which is still more translucent than the remaining portions of the paper. This area is rendered less translucent or opaque relative to the paper by curing the mark which has been contacted with water or the aqueous sizing solution. This can be done in various ways, preferably by heating methods such as moving the web of paper over hot dryer rolls which are maintained at temperatures below the level at which the paper would be charred or otherwise damaged. Various other means may be used in this heating step, such for example as hot air or infra-red heat. While the entire sheet is preferably heated, localized heating of the mark is possible such as by a limited stream of hot air.

It is believed that the water content of the aqueous sizing solution contributes to the reduced light transmission and the raised character of the opaque area. In any event the sizing agent, when used, is part of the opaque area. The light transmission of the opaque area is significantly reduced as measured by the Bausch and Lamb opacimeter, B&L Optical Co., Rochester, New York. This reduction is at least about 1% as compared with the light transmission of the original paper. This reduction may vary, and may depend on the particular impregnating materials and the variation within any particular impregnating materials. This reduced light transmission is in contradistinction to the increased light transmission of a chemical watermark which has not been treated with a sizing solution.

The opaque area is raised relative to the original surface or thickness of the paper as determined by caliper measurements made with a unit known under the trademark TMI, model 549M Micrometer Testing Machines, Inc., Mineola, Long Island, N.Y. The caliper rise is about at least 5% of the original paper, but may rise to about 7%, and even substantially thereover. Again, this may be due to the nature of particular impregnating materials. This increase in thickness of the opaque area is in marked contrast to the chemical transparent area obtained without treatment with water or the sizing solution. It is seen that the opaque area is characterized by reduced light transmission and a rise in thickness of the paper, on the inclusion of an aqueous sizing solution in place of water. The sizing agent, when used, is a part of the opaque area and this is an important feature in view of the advantage of sizing the paper as well as obtaining the opaque area. The sizing agent does not detract from the desirable features of the opaque area.

Some examples are presented to illustrate various ways of practising the invention, but such examples are only illustrative and are not intended as exclusive embodiments.

EXAMPLE 1

A liquid composition, containing an epoxy impregnating compound is prepared from the following ingredients and amounts:

Ingredients	Parts by Weight
Epoxy resin (Dow Der 332)	5
Epoxy hardener (Dow experimental hardener X-2654.4)	1
"Methyl Carbitol" (Carbitol is a Registered Trade Mark) (diethylene glycol monomethyl ether)	4.5

A small metered amount of liquid composition is deposited on the surface of a foot square piece of 1/2" thick plate glass. The composition is spread uniformly over the surface with a hand roll consisting of an engraved roll bearing 75 depressions per inch and fitted with a handle. A die or hand stamp or rubber-like material having inscribed on the face thereof a typical watermark design is first pressed against the wet film of the composition on the glass and then stamped on the paper sheet. Before the epoxy resin is cured by the curing agent into a hard film, the sheet of paper is totally immersed in a bath containing 8% chlorinated starch in water, said bath being maintained at 80° to 150°F. The sheet of paper is removed and subjected to heating by hot air until the paper is dry.

The Dow 332 epoxy resin and the Dow hardener for said epoxy resin are supplied by the Dow Chemical Company of Midland, Michigan. The Methyl Carbitol solvent is supplied by Union Carbide.

EXAMPLE II

Ingredients	Parts by Weight
Epoxy resin (Dow Der 332)	5
Pyromellitic dianhydride	1
"Methyl Carbitol"	4½

The above liquid composition, with epoxy resin impregnating compound, is manipulated in the same way described for Example I to obtain a shadow chemical watermark.

The pyromellitic dianhydride, which is supplied by the DuPont Company, has been found to be a preferred curing agent or hardener for the epoxy resin since likelihood of possible discoloration of a chemical watermark is even further reduced. The pyromellitic dianhydride is a preferred curing agent, not only for the shadow chemical watermarks but for the translucent chemical watermarks.

EXAMPLE III

Ingredients	Parts by Weight
Epoxy resin Dow Der 332	5
Borax epoxy curing agent No. 120	1
"Methyl Carbitol"	4½

The above formulation is manipulated in same manner as disclosed in Example I to obtain chemical watermarks of desirable properties. The borax curing agent is supplied by the U.S. Borax Company.

EXAMPLE IV

Ingredient	Parts by Weight
Polyester resin (Koplac D—3000—1500)	10.0
Benzoyl peroxide	0.2
"Methyl Carbitol"	10.2

The polyester resin is supplied by the Kopper Company and the peroxide curing agent by Matherson, Coleman and Bell. The above formulation is manipulated in the same manner as disclosed in Example I to obtain a shadow chemical watermark of desirable properties.

EXAMPLE V

Ingredient	Parts by Weight
Epoxy resin, Epon 812 (Shell Chemical Company)	6
Epon Curing Agent H—3 (Shell Chemical Company)	3
"Methyl Carbitol"	9

The above ingredients are mixed and a portion of a few ml is deposited at the top of a sheet of paper. A gravure roller of a width wider than the paper is pulled through the deposited liquid composition causing the composition to be laid down on a sheet of dry or finished paper. Within 3 minutes the entire sheet is immersed in a bath containing 8% chlorinated starch and held at 80°F to about 150°F. The excess starch solution is removed and the sheet is exposed to a stream of hot air until the sheet is dried and becomes opaque relative to its original condition.

In like manner the liquid composition of Example I through IV are used in the process of Example V to opacify entire sheets of paper.

The liquid compositions and steps disclosed in Example I through V are used with finished paper which is either surface sized previously or not surfaced sized. An important advantage of the process is that the paper which is not surface sized may be simultaneously surface sized and rendered opaque. The opaque area, of course, may be limited as for a shadow mark, or may extend throughout the entire surface of the finished paper sheet. A previously sized paper will receive an additional sizing treatment which may be cumulative or complementary to an original sizing to obtain desired sizing properties.

The following examples illustrate the use of ordinary water alone in the step of contacting the impregnating materials before such have cured into a hardened form.

EXAMPLE VI

The following ingredients and amounts are mixed:

Ingredients	Parts by Weight
Epoxy resin, Epon 812 (Shell Chemical Company)	6
Epon Curing Agent H—3 (Shell Chemical Company)	3
"Methyl Carbitol"	8

A few ml of the liquid composition are deposited at the top of a sheet of paper. A gravure foller of a width wider than the paper is pulled through the deposited liquid causing the solution to be laid down on the dry or finished paper. Within two minutes, the sheet is immersed in a bath of tap water held at room temperature. Thereafter, the sheet which is entirely wetted is dried in an oven at about 300°F for about one minute. The entire sheet is rendered opaque relative to the original condition of the finished sheet.

The compositions of Examples I through IV are manipulated by the same steps as described in Example VI to opacify an entire sheet of paper, and to impart shadow marks only to a portion of a finished sheet of paper.

The following Table I presents data comparing light transmission through a translucent chemical mark which is cured into a hardened form without water treatment, a shadow chemical mark prepared according to this invention, and a control portion of untreated paper. The shadow marks are formed by using the liquid compositions disclosed in Example III (liquid Composition A) and Examples V and VI (Liquid Composition B). All the shadow marks tested in Tables I and II formed by using ordinary tap water at substantially room temperature to wet the impregnating material before they have cured into a hard form. Each of these measurements are made on the same sheet of a selected weight. Light transmission is measured with a Bausch & Lamb opacimeter, B & L Optical Co., Rochester N.Y. The figures in the first three columns represent the per cent of light which did not pass through the paper.

The column identified by "Basic Weight-lbs" refers to the thickness of the paper used. The weight figures are determined from a ream of 500 sheets of paper, each sheet having a dimension of 17" × 22". The higher the weight, the thicker the paper. The symbol C refers to the light transmission of the paper control, the symbol O refers to the light transmission of the opaque area. The column entitled O—C refers to the difference between these light transmissions, and the last column in the Table 1 refers to the per cent increase in opacity or reduction in light transmission.

TABLE 1

Basic Weight lbs	Translucent Mark	Paper Control	Opaque Mark	O—C	$\frac{O—C}{0} \times 100$ (Percent)
LIQUID COMPOSITION A					
16	61.2	78.0	79.2	1.2	1.51
20	71.1	84.5	85.7	1.2	1.40
24	77.6	86.7	88.0	1.3	1.48
28	74.2	88.6	90.1	1.5	1.66
32	81.2	88.6	90.1	1.5	1.66
36	83.1	89.6	91.1	1.5	1.65
LIQUID COMPOSITION B					
9	37.5	55.1	61.0	5.9	9.67
13	58.0	71.0	73.0	2.0	2.73
16	64.2	76.2	80.2	4.0	4.99
20	72.2	82.2	85.0	2.8	3.29
24	81.2	87.2	88.3	1.1	1.25
28	76.3	84.8	87.0	2.2	2.52
32	80.2	87.8	89.8	2.0	2.23
36	85.5	90.2	92.0	1.8	1.95
CONVENTIONAL SHADOW MARK FROM DANDY-ROLL					
20		89.0	96.0	1.6	1.77

The following Table II presents the raised caliper data for the shadow marks imparted to various weight paper. As in Table 1, liquid compositions A and B are, respectively, the formulations of Examples III and V, and ordinary tap water is used to make the impregnating materials opaque. An electronic caliper device is used, namely, TMI, model 549M micrometer, Testing Machines, Inc., Mineola, Long Island, New York. The machine is sensitive to 0.1 mil and allows estimations to 0.01 mil.

TABLE II

Basic Weight lbs.	Translucent Mark R	Paper Control C	Opaque Mark O	O—C	$\frac{O-C}{0} \times 100$ (Percent)
LIQUID COMPOSITION A					
16	3.5	3.5	4.1	.6	14.63
20	4.6	4.7	5.4	.7	12.96
24	5.5	5.7	6.4	.7	10.94
32	6.2	6.4	7.2	.8	11.11
36	6.9	7.0	7.6	.6	7.89
LIQUID COMPOSITION B					
9	2.3	2.1	2.3	.2	9.70
13	3.1	2.9	3.1	.2	6.45
16	3.6	3.6	3.9	.3	7.69
20	4.8	4.7	5.3	.6	11.32
24	5.7	5.4	5.9	.5	8.47
28	5.4	5.6	6.0	.4	6.67
32	6.1	6.2	6.6	.4	9.09
36	7.8	6.9	7.4	.5	6.76

The paper articles prepared with the chemical shadow watermark of the invention are serviceable for at least the useful life of the paper. By this it is meant that the opaque area is substantially resistant to the mechanical abrasion encountered by paper such as erasing. Such area is, of course, ink receptive in substantially the same way as the remaining portions of the paper, and resists discoloration for at least desirable periods of time. The useful life of paper may be variously measured, and the substantial majority of stationery bond, for example, has a relatively short useful life. Nonetheless, such opaque areas retain desirable properties even after a stationery bond has been stored or filed for substantial periods.

An advantageous way to practice the invention for making shadow marks calls for sizing the entire sheet of the paper. It will be realized, of course, that such is not necessary since a previously sized paper may be converted into a paper article with the shadow chemical watermark. In such a case, the liquid composition with the impregnating materials is imparted to only a portion of the paper, and substantially only that portion may be contacted with the sizing solution. If desired, previously sized paper could be again contacted in its entirety with the sizing solution.

Reference has been made to using sizing solutions and these are intended to include any of the various size tub agents in a water solvent. Understandably, such sizing tub agent will commonly be selected from the starches which are widely used in sizing paper. If it is not desired to simultaneously size the paper or to use a sizing solution in any way, then water may simply be used in its place. This leads to an even more simple and economical method.

WHAT WE CLAIM IS:—

1. A paper article having an area comprising a cured, thermosetting resin, the resin being absorbed into the paper and being raised at least 5% relative to the original thickness of the paper, and the area having an opacity which is increased at least 1% relative to the original light transmission of the paper.

2. A paper article as claimed in claim 1 in which the thermosetting resin is an epoxy resin which has been cured with an epoxy curing agent.

3. A paper article as claimed in claim 1 or 2 in which the opaque area includes a sizing agent.

4. A paper article as claimed in claim 3 in which the paper sheet is sized with the same agent as used in the opaque area.

5. A paper article as claimed in any one of the preceding claims in which the opaque area comprises a limited portion of the paper surface and is a shadow mark in the form of a selected design.

6. A paper article as claimed in any one of claims 1—4 in which the opaque area extends throughout the entire surface of the paper sheet.

7. A paper article as claimed in any one of the preceding claims in which the thermosetting resin is synthetic.

8. A paper article as claimed in claim 1 substantially as herein described.

9. A method of chemically opacifying paper, which comprises applying to the surface of the paper an area of a liquid composition containing a thermosetting curable resin, a curing agent therefore, and an organic solvent; contacting said area with water before said thermosetting resin has hardened; and curing said thermosetting resin on said paper until said thermosetting resin hardens.

10. A method as claimed in claim 9 in which the hardened thermosetting resin is raised at least 5% relative to the original thickness of the paper, and in which the opacified paper has an opacity which is increased at least 1% relative to the original light transmission of the paper.

11. A method as claimed in claim 9 or claim 10 in which the water is in a sizing solution containing a sizing agent.

12. A method as claimed in claim 11 in which the paper is contacted with the liquid composition and the sizing solution so that the paper is sized simultaneously with contacting the liquid composition on said sheet.

13. A method as claimed in any one of claims 9—12 in which the liquid composition is applied to the entire surface of the paper, and then the water is applied to the entire paper to render the entire paper opaque.

14. A method as claimed in any one of claims 9—12 in which the liquid composition is applied only to a limited portion of the paper surface in a selected design, and then water is applied to at least that limited portion to obtain a shadow mark.

15. A method as claimed in any one of claims 9 to 14 in which the thermosetting resin is an epoxy resin.

16. A method as claimed in any one of claims 8 to 15 in which the thermosetting resin in synthetic.

17. A method as claimed in claim 9 substantially as hereinbefore described.

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