

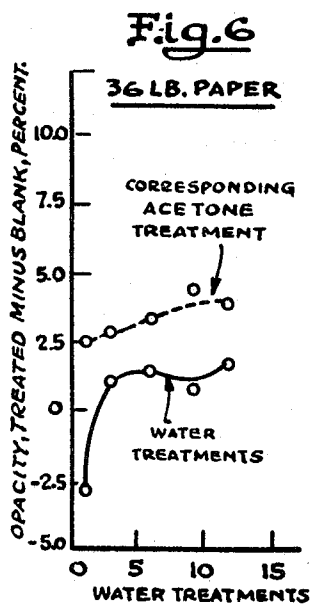
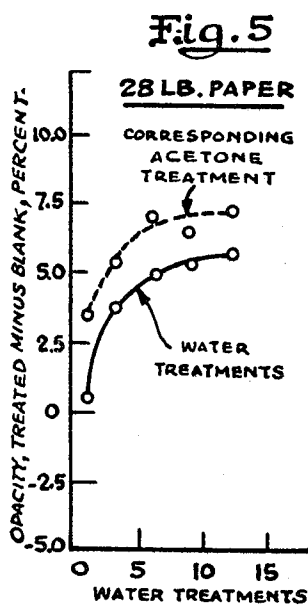
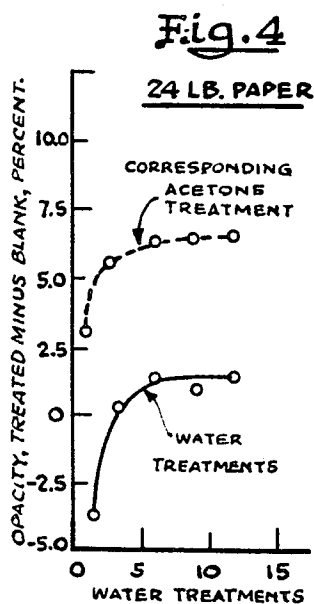
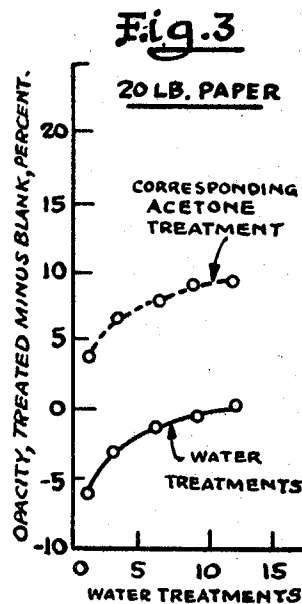
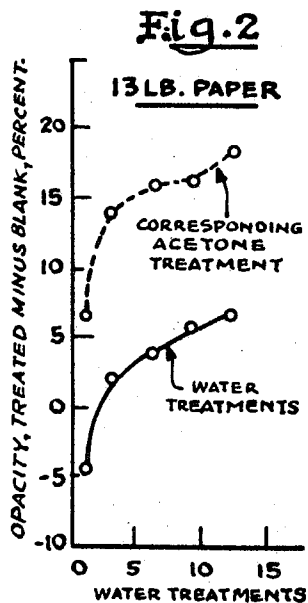
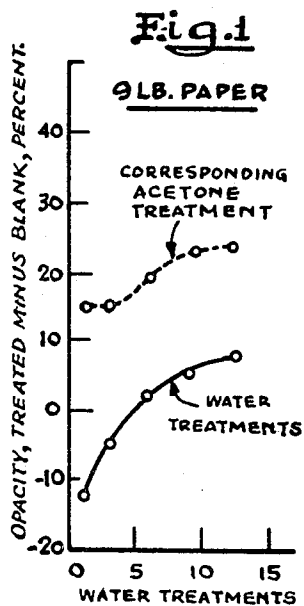
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METHOD OF RENDERING SHADOWMARK OPAQUE BY SOLVENT TREATMENT

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METHOD OF RENDERING SHADOWMARK OPAQUE BY SOLVENT TREATMENT

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U.S. Cl. 117—37

29 Claims

ABSTRACT OF THE DISCLOSURE

A paper article is provided with areas which are opaque relative to the original light transmission of the paper. The opaque area may extend throughout the entire paper or may be a limited area of a selected design to attain a shadowmark. The opaque area is provided in an improved manner by employing an organic solvent treatment step to subsequently contact a resin and water treated area on the paper. A resin is used which can be laid down as a wet film and which impregnates the paper fibers or paper web. The resin is applied in a liquid composition which may or may not include an organic solvent and a chemical curing agent. A series of steps provide applying the resin to the paper, contacting the resin with water, drying the paper, and then contacting with an organic solvent. A plurality of successive water treatment, drying and organic solvent treatment steps may be selected in some embodiments to develop or enhance the appearance of the opaque area.

This invention relates to a method of obtaining paper articles having opaque areas, and the invention particularly relates to a method of obtaining such opaque areas in an improved manner.

It is known in the art to prepare sheets of paper having areas which are rendered translucent in whole or in part by contacting the sheets of paper with chemical impregnating materials. See, for example, U.S. Letters Patent Nos. 3,293,062, 3,140,959 and 3,085,898.

The liquid resin compositions are applied to the surface of the paper, and the resin is then hardened or dried, whereupon a translucent area is obtained. When the area is limited only to a portion of the entire surface, and when a fanciful design is formed, then the translucent area may be considered as being a watermark. Such a watermark may appear to be of the same quality as conventional watermarks, and they may also be referred to as simulated watermarks or chemical watermarks. This is a recognized advance in the paper art because high quality watermarks are obtained which have economic advantages as a result of the substantially lower costs incurred in producing the marks. Such marks may be applied or printed on paper in smaller runs after the paper is formed. This is in contradistinction to the conventional watermarks which are made by a dandy roll during the paper-forming stage.

Shadowmarks are formed on paper as paper sheets for the same general purposes as are watermarks. Such reasons include the attainments of quality, identification, esthetics and the like. The conventional shadowmarks are opaque relative to the balance of the paper as distinguished from watermarks which are translucent relative thereto. Shadowmarks have also been formed by a dandy roll during the paper making stage, and such dandy rolls have a recess or well in which the paper fibers collect to make the opaque area. Watermarks are conventionally made during the paper-making stage by a raised die on the dandy roll which spreads the paper fibers.

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This application is a continuation-in-part of applicant's copending application. Ser. Nos. 525,343 and 536,487 now abandoned, both filed Feb. 7, 1966.

It is one important object to provide an improved method for attaining opacity of areas by first contacting a deposited resin on paper with water, and then contacting the resin-applied area with an organic solvent.

Yet another important object of the invention is to use the foregoing organic solvent step to enhance the development of desirable opaque areas so that a smaller number of successive water treatment steps may be employed in some embodiments to attain the desirable opaque areas.

Yet another important object of the invention is to provide an improved method wherein successive series of steps may be used to obtain desired opaque areas, wherein each series includes applying a resin to the surface of the paper, wetting the paper, and then contacting the deposited area with an organic solvent.

It is another important object to provide an improved method of the foregoing type to opacify entire sheets of paper.

It is another important object to provide an improved method of the foregoing type to form opaque areas of limited extension to attain shadowmarks on paper.

Objects such as the foregoing are attained by the invention of the following disclosure, as well as still other objects which may occur to practitioners. The disclosure includes drawings of FIGURES 1-6 which illustrate how a liquid impregnating composition of the invention may more effectively develop opacity after single organic solvent treatments following varying numbers of water treatment steps.

Applicant's parent application, previously cited, and a copending application, filed of even date herewith, teach that opaque areas are made on sheets of paper by applying a liquid composition containing one or more resins to the surface of the paper, and then contacting with water. The composition is in a liquid form to facilitate application, and the composition is of a viscosity sufficiently low to allow impregnation of the paper fibers or the paper web by the resin. The liquid composition may be used to opacify entire sheets of paper, whereupon only excessively low viscosities are avoided which would cause the composition to pass through the paper. The liquid composition may also be used to make opaque shadowmarks, whereupon the viscosity is maintained sufficiently high to retain the design which is applied to the surface of the paper while still allowing impregnation of the paper fibers or paper web. The water treatment step leads to an area on the surface of the paper which is opaque relative to the original condition of light transmission of the paper, and which is raised relative to the original surface of the paper. It is a feature of the foregoing method that a plurality of successive water treatment and drying steps lead to the development of the opaque area when using some liquid compositions which do not lead to a satisfactory opaque area following a single water treatment step.

The present invention provides that the opaque areas are developed in an improved manner by contacting deposited resin on the paper with an organic solvent after the water treatment step. It has also been found that the preferred step is to contact the treated area with the organic solvent after the paper has been dried following the water treatment step. If the organic solvent is applied prior to the water treatment step or before the paper has been dried after water treatment, the laydown of the resin on the paper may be adversely affected. The resin will be dissolved or thinned out so that the desired opacity or definition of the opacity is not attained. The

use of the organic solvent treatment step results in the area becoming more opaque, as well as having a better definition of opacity when shadowmarks are formed on paper. A successive number of organic solvent treatment steps may be used after a successive number of water treatment steps for some embodiments to improve the development of opacity.

It is not known with certainty how the resin of the liquid composition is altered by water contact and organic solvent contact. It is clear that a plurality of interfaces are formed in the opaque area because the area is raised and because light transmission has been significantly changed relative to the original light transmission of the paper. These "interfaces" may be voids or water-resin interfaces or solvent-water-resin interfaces, or they may have a still different physical or chemical composition. Without intending any particular identification or characterization, it is nonetheless accurate and meaningful to refer to a plurality of such interfaces in the altered resin which renders the treated paper area opaque and raised relative to the original condition of the paper. Some sort of incompatibility may result between the resin, water and solvent following one or more steps of contacting the resin with the water and a following treatment with solvent. It is believed that, in some instances, the opacifying interfaces build up to a measurable or recognizable level following a plurality of successive water treatment and organic solvent treatment steps. Be that as it may, the practitioner who follows the teachings of this disclosure will readily recognize when a satisfactory opaque area is formed after one or after a plurality of successive water treatment, drying and organic solvent treatment steps.

When reference is made to "impregnating paper fibers or paper webs," it is intended to mean that the resin in the liquid composition moves between the paper fibers or into the paper fibers, or both. The important point is that the resin should not conglomerate or puddle on the surface of the paper because an undesirable quality of the opaque area would result if any at all. It is not known how much of the resin actually penetrates into the fibers or merely collects between the fibers, but an operable impregnation occurs in the sense that the resin moves into the paper and is retained within the paper. The liquid composition, therefore, has impregnating materials which are laid down as a wet film.

The liquid composition may consist of a resin alone which is in fluid form, or it may include a mixture of resins to effect greater fluidity. For example, it may include a plasticizer which acts as a diluent. The liquid composition may also contain an organic solvent in many of the preferred forms to provide good, workable fluidity, and to further effect a neat impregnation and hardening of the resin following a drying step or a curing step. The liquid composition may contain a chemical curing agent for the resin in many preferred forms, but a chemical curing agent may not be necessary for many other forms. Reference may be made to resin forms undergoing "drying or hardening," and these terms are used in an equivalent manner to include the concepts of air-curing by chemical agents, catalysts, hardeners or the like. The term "hard" may be used more meaningfully relative to air curing, but in any event, the terms are used equivalently to assert that a resin in a liquid composition is converted into a hard film or layer which is characteristic of resins which are conventionally air-cured or chemically cured. Such terms will have limited meaning for materials which do not harden into a film, such as some organic solvents or plasticizers. When dealing with resins which are cured to a dry, hard film, the water treatment step is made before the resin cures or hardens. When the liquid composition contains such a resin and an organic solvent for the resin, the water treatment step is preferably made while the composition remains wet on the paper, that is, before all the solvent has thus been removed. The amount of organic solvent which

is removed from such a liquid composition may be a major amount of more than 50% of the original amount and say, less than about 90%. As stated, the paper is dried, following the water treatment step, before the organic solvent treatment is effected. The organic solvent treatment step is preferably performed as soon as possible following the drying step. It is not required nor desired that the drying step be extended, but the drying step should remove substantially all of the water, say, down to about 2% in the paper. In general, sheets of paper have been effectively dried by passing them over heated, felt-covered drum driers having a surface temperature of about 78–80° C. The paper sheets are effectively dried when they are brought into contact with such heated drums for short periods of time of about 60–120 seconds. Likewise, hot air or heating ovens may be employed for correspondingly brief periods of time to remove substantially all of the water.

Undue delay between the drying and the subsequent organic solvent treatment step should be avoided, especially with certain resins such as the thermosets which would substantially resist alteration by interface modification or formation by the organic solvent. It is therefore a preferred general practice to execute the organic solvent treatment step right after the water drying step. It should, however, be understood that with other resins interface formations or modification may occur with organic solvents even following substantial hardening or curing. One or more successive organic solvent treatment steps may be used with intervening drying, but in many instances a single solvent treatment is adequate to obtain opacity having good definition. The organic solvent treatment may be applied after several water treatments, and more than one successive solvent treatments may then be applied. Once a solvent treatment is effected, however, no further water treatments are prescribed. In practice, the time delay or lag between successive steps of water wetting, drying, water rewetting, redrying and solvent contact may be varied to attain the preferred conditions in operation. Skilled practitioners will readily recognize by trained observation and standard measurement when an acceptable opaque area has been attained.

Opaque shadowmarks may be formed on a sheet of paper, for example, by a printing step where a liquid composition is printed as a wet film on this surface. This may be conventionally done by hand-stamp, elastomeric die on a roller or by a similar letter press technique. While a printing step is the preferred form, the wet film of liquid composition may be applied otherwise as by brushing or spraying the liquid compositions through a stencil. Other methods of application will occur to practitioners in this art. The paper may be made entirely opaque by dipping the sheet in the liquid composition. A change of the liquid composition may also be deposited on surfaces of paper, followed by pulling a roller or the like through the deposited charge until the entire surface is covered with a film of the liquid composition.

Whatever the identity of the resin material which is deposited, it is preferred that the wet film undergo some drying before the first water treatment step. A sheet of paper with the wet film may be passed, for example, over a hot felted drum dryer for 60 seconds, said drum being held at 79° C.

The water treatment may be performed by dipping, spraying, fogging, providing a high humidity by environment or by other means. The organic solvent treatment may be attained by similar procedures.

As a general illustration, the water treatment step is applied after about a minute or two following application of the liquid composition to the paper, so that adequate impregnation occurs. When such wetting is attained by dipping, the sheet may be nipped between rollers or the like to remove excess water, then dried on a felt covered drum dryer at temperatures of about 80° C. for about a minute or two. The sheet can then be immediate-

ly dipped in an organic solvent, nipped between rollers or the like to remove the excess organic solvent, and dried in the same way for about a minute or so.

Many types of organic solvents are operable in the practice of the invention, and representative members have been shown. Such types include the aliphatic hydrocarbons, the halogenated hydrocarbons, alkanols, the ketones, esters of monocarboxylic acid and medium length carbon alcohols, the hydrocarbon ethers, substituted and unsubstituted cyclic hydrocarbons which may be saturated or unsaturated, polyhydroxyl alcohols, esters of alcohols and dicarboxylic acids, and alkyl anhydrides. Practitioners may find that still others may be used.

Reference has been made and will be made to "resins," and such term is intended to cover materials which can be applied as a wet firm which can impregnate paper fibers on the paper web, and which materials may be contacted with one or more water treatments to opacify the paper. Such paper impregnating materials may include natural and synthetic resins, plasticizers, some organic solvents, esters, and other materials which will be, in part, described. The natural resins may be further substituted or modified, such as rosin; a hydrogenated methyl ester rosin; a partially decarboxylated rosin; an ethylene glycol ester of hydrogenated rosin; hydrogenated abietate esters with various mono-, di- and trialkyl glycols or mixtures thereof; and others. These natural resins may be combined with solvents or plasticizers to desirably attain an operable viscosity of the liquid composition.

The liquid composition may even be a solid which is softened or liquified by lower temperatures such as Aquapel, an alkyl ketene dimer supplied by the Hercules Powder Co.

Still other resins are various esters of polyols with saturated diacids and unsaturated diacids. These may be polyesters of glycols with dicarboxylic acids which are saturated such as adipic, pimelic, azelaic and the like. They may also be glycols esterified with unsaturated dicarboxylic acids, such as succinic or the like. Some representative esters are polypropylene adipate, triethylene glycol hydroabietate and the like. Such esters may also be dialkyl sulfosuccinates, sucrose acetate butyrate and sucrose acetate isobutyrate as disclosed in U.S. Letters Patent No. 3,085,898 of the present assignee.

Thermosetting resins are successfully used, and representative resins of this type are disclosed in U.S. Letters Patent No. 3,140,050 issued to the present assignee. Such resins include a urea and melamine formaldehyde, polyester, phenolic resins and epoxy resins. Other thermosetting resins are the alkoxy substituted melamine resins such as hexamethoxymethylmelamine. Such resins may be combined with a variety of organic solvents or plasticizers to effect the desired viscosity. They may include ketones such as methyl, isobutyl ketone, esters such as dibutyl phthalate, various alkylene glycol alkyl ethers such as ethyleneglycol monomethyl ether, and a large number of other solvents. Representative solvents and plasticizers are also listed in the foregoing U.S. Patent No. 3,140,050.

Chemical curing agents are preferably used for the foregoing thermosetting agents and such agents are well known in the art. While a preferred liquid composition would include a thermosetting resin, a solvent and a curing agent, it should be noted that the solvent and curing agent may be omitted. Some thermosetting resins or combinations of resins may be sufficiently liquid to be applied to the sheet of paper in the form of a design, and then be contacted with water and the organic solvent. Certain epoxy resins have been used without a curing agent and without a solvent. Reference is likewise made to the foregoing U.S. Patent No. 3,140,050 for particular examples.

The resin esters may also be polymeric plasticizers such as the material provided under the name of Eastman NP 10 supplied by the Eastman Chemical Products Company. Likewise, the ester may be a monomeric plasticizer used in conjunction with some higher molecular weight poly-

ester to provide dilution or solvation. These plasticizers may include diesters of phthalic esters and lower monohydric alcohols, such as the dimethyl, diethyl, or the like. Other plasticizers or solvent esters may include cyclohexanone. Such monomeric plasticizers are preferred as diluents for polyesters or other resins to effect the desired fluidity. The monomeric esters may, however, be useful for developing an opaque mark by themselves, and one such ester is the monomeric epoxy supplied under the trade name "Monoplex MS 73" by the Rohm & Haas Company.

Still other resins may be used such as aryl sulfonamides diluted with a plasticizer such as dioctyl phthalate. Thermoplastic resins also find useful application in this invention such as acrylonitrile butadiene styrene or ABS. It will be apparent that other thermoplastics may be of the allyl type, of the acrylic type, of the amide type, of the fluoro type, of the vinylchloride type and still other types. Still other resins will include the cellulose such as the acetate, propionate, or ethyl cellulose resins. Among other operable materials are film formers and paper impregnators such as triacetin, diethyleneglycol monomethyl ether and N methyl 2-pyrrolidone.

Some examples are now presented, but they are intended to be only illustrative, even though they include embodiments now contemplated to best meet various purposes of the invention.

Example 1

A liquid composition is prepared by mixing the following ingredients and amounts.

Ingredients:	Parts by weight
Epoxy resin (Iso Chem Res Trans Flex)-----	10
Epoxy curing agent (EPI Cure 8771)-----	3
Methyl Carbitol (diethylene glycol monomethyl ether) -----	10

The epoxy resin is obtained from the Iso Chem Resin Company of Lincoln, R.I., the epoxy curing agent is obtained from Celanese Resin Company of Louisville, Ky., and the Methyl Carbitol from Union Carbide. The ingredients are mixed to attain their liquid composition, and a small metered amount of said liquid composition is deposited on the surface of a foot sq. piece of 1/2 inch 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 of rubber-like material having inscribed on the face of a typical watermark design is first pressed against the wet film of the composition on the glass and then stamped on a paper sheet. About three minutes later, the sheet of paper is totally immersed in a bath of water maintained at room temperature. The sheet of paper is withdrawn, the excess water is removed by a nipping operation, and the paper is subjected to heating by contact with a hot felted dryer maintained at 80° C. for 60-120 seconds.

Following a single water treatment, the opacity of the treated area may actually be decreased as compared to the original light transmission of the paper. The paper, however, is dipped in acetone following said drying and then again dried with hot air as before. The opacity of the area, following such solvent treatment, is increased substantially relative to the opacity of the area after the water treatment.

Another sheet of paper has the same liquid impregnating composition applied in the form of a selected design. The sheet is dried by passing over a hot felted dryer maintained at 80° C. for 60 seconds. The sheet is then dipped in water and nipped between a brass roller and a rubber covered roller to remove the excess water. The wet sheet is then passed over the hot felted dryer twice, each pass taking 60 seconds to execute. The sheet is then dipped in water a second time and dried as in the previous sequence of dipping and drying. Following these two

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water treatment and drying steps, the sheet is dipped in acetone, nipped between the brass and rubber rollers, and then passed twice over the hot felted dryer held at 80° C., each pass requiring 60 seconds.

Example 2

A liquid composition is prepared by mixing the following ingredients in amounts stated.

Ingredients:	Parts by weight
Epoxy resin.....	7½
Methyl Carbitol.....	2½

The above liquid mixture contains the same epoxy resin used in Example 1, and this mixture is processed according to the steps of Example 1. Two separate sheets are impregnated with liquid composition. The first sheet is given one water treatment followed by one acetone treatment, and the second is given two successive water treatments followed by one acetone treatment, as described in Example 1. Following one water and one acetone treatment, the opacity is increased over the opacity recorded following the first water treatment alone. After two successive water treatments followed by one acetone treatment, the opacity is increased over the opacity recorded following the second water treatment, and, the opacity is increased over the light transmission of the original paper.

Example 3

A liquid composition is prepared by mixing the following ingredients in amounts stated.

Ingredients:	Parts by weight
Polyester resin (Koplac D 3,000-1,500).....	10
Curing agent, benzoyl peroxide.....	½
Methyl Carbitol.....	10

The polyester resin is obtained from Koppers Chemical Co. The liquid mixture is processed by the steps of Example 1 and is used to impregnate two sheets of paper which are then treated as in Example 1. After one acetone treatment, the opacity is increased relative to the light transmission following one water treatment and generally, is increased relative to the light transmission of the original paper. After the acetone treatment following two successive treatments, the opacity is increased over the light transmission recorded after the second water treatment, and is increased to a more significant extent relative to the light transmission of the original paper.

Example 4

A liquid composition is prepared by mixing the following ingredients in amounts stated.

Ingredients:	Parts by weight
Polyester resin.....	7½
Methyl Carbitol.....	2½

The above liquid composition contains the same resin used in Example 3, and is processed according to the process steps of Example 1. Two sheets are impregnated and are then separately heated as described in Example 1. After one acetone treatment and two preceding water treatments, the opacity is increased relative to the original light transmission of the paper, and is significantly increased relative to the light transmission following the second water treatment.

Example 5

A liquid composition is prepared by mixing the following ingredients in amounts stated:

Ingredients:	Parts by weight
Hexamethoxymethylmelamine.....	10
Curing agent (EPI cure, 8771-Jones Dabney Co.)	3
Methyl Carbitol.....	2

The resin is obtained from the American Cyanamid Co. under the trademark Cymel 301.

A plurality of paper strips which are 4¼" x 11" are

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immersed in the above liquid impregnating composition, then nipped between brass and rubber covered rollers, and dried by passing over a hot felt covered drum dryer at 70° C. for 60 seconds. The dried strips are then dipped in water, nipped as in the resin treatment step, and dried by being passed twice over the drum dryer for a total of 120 seconds of drying time. After the first water treatment, the paper is again dipped in water, nipped and dried. The paper strip is then dipped in acetone and dried by passing twice over the drum dryer for a total drying time to 120 seconds. The opacity of the paper after the second water treatment increases relative to the original paper, and the opacity after the acetone treatment increases substantially relative to the original paper and relative to the measured opacity after the second water treatment.

Example 6

A liquid composition is prepared by mixing the following impregnating materials in the amounts listed.

Ingredients:	Parts by weight
Hexamethoxymethylmelamine.....	7½
Methyl Carbitol.....	2½

The same resin is used as in Example 5. The above liquid composition is applied to the surface of paper strips as described in Example 5 which are then wetted with water and dried. The strips are wetted with acetone and dried by procedural steps similar to that described in Example 5.

After the first water treatment, the opacity is slightly increased relative to the original condition of light transmission of the paper, and after one acetone treatment, the opacity is substantially increased relative to the original condition of light transmission and relative to the opacity measured after the first water treatment.

The liquid compositions of the foregoing Example 1-6 are used, respectively, in following Tables I-VI to cover entire paper strips as described particularly in Example 5. Following one and two water treatments and drying steps, the strips are treated with a variety of solvents and with a variety of solvent mixtures. The representative organic solvents employed are listed below together with the corresponding symbols which will be used in the following tables:

Names of organic solvents:	Symbol
Acetic anhydride.....	AcAn
Acetone.....	A
Amy acetate.....	AmAc
Ethyl alcohol.....	EA
Ethylene glycol.....	EG
Carbon tetrachloride.....	CT
Heptane.....	H
Methyl carbitol.....	MC
Toulene.....	T
Trichloroethane.....	TCE
Eylene.....	X

In each of the tables the area was opacified by using the listed solvents and following the process steps of Example 5 which provides for one organic solvent treatment after one and after two water treatment steps. All the opacity or light transmission measurements are made with a Bausch & Lomb opacimeter, B & L Optical Company, Rochester, N.Y. Each opacity measurement represents an average of three separate readings on spaced portions of a paper strip, that is, a blank or control strip, a strip after one water treatment and after a following single organic solvent treatment and a strip after two water treatments and a following single organic solvent treatment. The paper used in such tests is 9 lb. paper, 25% cotton (500 sheets, 17" x 22"/sheet).

Table I shows that a liquid composition containing an epoxy resin and a chemical curing agent for the resin leads to an opacity increase in each instance after the first solvent treatment relative to the first water treatment.

After a solvent treatment following two water treatments, the opacity increases, in each instance, over the light transmission of the original paper and over the measured opacity following the second water treatment.

the solvent treatments with respect to the light transmission measured after the corresponding first and second water treatments. After the first water treatment and one solvent treatment, about half the samples have an opacity

TABLE I

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Solvent	Blank	First Water Treatment	Solvent Treatment	Percent Change $100 \times (2) - (3) / (3)$	Second Water Treatment	Solvent Treatment	Percent Change $100 \times (5) - (6) / (6)$
A.....	54.5	43.8	66.5	34	50.7	68.3	26
CT.....	54.9	45.5	61.6	26	56.7	62.3	9
H.....	53.8	42.1	46.9	10	51.3	55.7	8
X.....	55.1	43.0	50.4	15	55.8	65.2	14
TCE.....	53.1	41.0	46.8	12	50.9	60.0	15
MC.....	52.6	35.8	49.3	27	45.7	61.7	26
T.....	54.0	36.5	36.0	-----	46.6	62.2	25
Am Ac.....	52.1	37.6	56.1	33	49.5	61.9	20
EG.....	54.5	36.9	61.7	40	46.3	61.2	24
1A:1H ₂ O.....	52.3	43.3	50.7	15	54.8	59.2	7
1EA:1H ₂ O.....	53.2	44.8	53.3	16	51.8	58.0	11
1CT:1H ₂ O*.....	54.3	42.2	50.0	16	52.1	58.0	10
1A:1CT.....	52.0	55.4	63.0	12	61.8	69.8	12
1A:3MC.....	53.1	35.8	59.0	39	46.6	65.2	29
1A:1MC.....	52.4	37.4	53.7	30	62.2	63.7	2
3A:1MC.....	54.9	42.2	49.5	15	61.6	69.3	11

* Immiscible mixture.

Table II shows that a liquid composition containing an epoxy resin but no curing agent leads to an increased opacity following organic solvent treatments, in every instance, over the corresponding first and second water

increase relative to the light transmission of the original paper; and after the second water treatment and one solvent treatment, all the samples show an opacity increase relative to the light transmission of the original paper.

TABLE III

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Solvent	Blank	First Water Treatment	Solvent Treatment	Percent Change $100 \times (2) - (3) / (3)$	Second Water Treatment	Solvent Treatment	Percent Change $100 \times (5) - (6) / (6)$
A.....	51.8	35.8	58.5	39	39.3	63.7	38
X.....	52.5	42.0	43.5	3	50.0	57.3	13
TCE.....	51.2	39.3	45.5	14	41.8	56.2	26
MC.....	54.5	39.2	60.5	35	42.5	64.2	34
T.....	53.0	61.0	56.8	10	53.2	59.2	11
EA.....	52.6	46.6	56.5	18	48.2	57.0	15
1A:1EA.....	54.4	44.9	54.3	17	46.9	59.0	21
1A:3MC.....	52.9	46.9	58.7	20	47.8	64.7	26
1A:1MC.....	52.6	43.3	52.0	17	48.3	60.5	20
3A:1MC.....	54.5	46.0	53.0	13	51.5	62.7	18

treatments. Except in a few instances, the solvent treatment after the second water treatment also leads to an increased opacity relative to the light transmission of the original paper.

The liquid composition of Table IV has a polyester resin but no chemical curing agent. In every instance, the opacity is increased after the solvent treatments relative to the light transmission after the first and second

TABLE II

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Solvent	Blank	First Water Treatment	Solvent Treatment	Percent Change $100 \times (2) - (3) / (3)$	Second Water Treatment	Solvent Treatment	Percent Change $100 \times (5) - (6) / (6)$
A.....	54.7	28.9	43.7	34	31.8	67.5	53
CT.....	51.7	28.7	34.1	16	31.0	65.3	53
H.....	54.1	26.5	39.5	13	29.2	33.2	12
X.....	54.3	27.5	36.6	25	30.5	69.3	56
TCE.....	52.7	27.8	42.6	35	29.7	40.0	26
MC.....	54.1	26.5	41.0	35	32.5	51.2	37
T.....	51.6	26.4	38.3	31	27.8	57.3	34
Am Ac.....	51.3	26.6	36.8	28	29.4	69.8	58
EA.....	53.2	28.4	31.4	10	31.2	60.5	48
1A:1CT.....	52.7	27.4	64.3	57	30.8	60.5	49
1A:3CT.....	54.7	29.7	61.8	52	34.1	67.0	34
1A:1MC.....	53.1	25.9	37.2	30	32.9	67.2	51
3A:1MC.....	52.3	29.4	64.4	54	33.5	67.5	50

Table III leads to opaque areas made with a liquid composition containing a polyester and a chemical curing agent. In every instance the opacity is increased after

water treatments. In every instance, the opacity of the treated area is increased after the water treatment and a following solvent treatment relative to the light transmission of the original paper.

TABLE IV

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Solvent	Blank	First Water Treatment	Solvent Treatment	Percent Change 100×(2)−(3)/(3)	Second Water Treatment	Solvent Treatment	Percent Change 100×(5)−(6)/(6)
A.....	53.9	33.3	63.2	46	35.5	65.9	46
MC.....	53.6	31.4	47.7	34	35.6	57.7	38
Am Ac.....	52.4	34.2	44.5	23	39.0	55.7	30
1H ₂ O.....	53.0	35.2	53.0	34	37.0	58.7	37
1A:1CT.....	54.4	33.9	62.2	45	37.3	63.7	41
1A:3MC.....	53.5	33.0	54.5	21	35.6	63.0	46
1A:1MC.....	54.5	34.4	56.0	28	37.7	63.5	41
3A:1MC.....	54.3	31.1	50.3	38	34.8	65.0	44

The liquid composition used in foregoing Table V contains hexamethoxymethylmelamine and a chemical curing agent. In every instance the opacity is increased after the solvent treatment steps relative to the light transmission of the treated area after the first and second water treatment steps. The opacity of the treated area is increased in most of the instances after a first water treatment and following solvent treatment relative to the light transmission of the original paper, and such opacity is increased in every instance following the second water treatment and following solvent treatment.

example, a representative embodiment is illustrated employing a sizing solution.

Example 7

A liquid composition is prepared from the ingredients of Example 1 and treated by similar process steps. However, before the epoxy resin is cured into a hard film, the sheet of paper is totally immersed in a bath containing 8% chlorinated starch and water, said bath maintained at 80° F. to 150° F. The sheet of paper is removed and subjected to heating by hot air until the paper is dry, say

TABLE V

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Solvent	Blank	First Water Treatment	Solvent Treatment	Percent Change 100×(2)−(3)/(3)	Second Water Treatment	Solvent Treatment	Percent Change 100×(5)−(6)/(6)
A.....	52.2	45.6	59.5	23	57.6	68.3	16
CT.....	54.8	44.3	59.1	25	57.9	66.7	13
H.....	53.4	44.8	45.5	2	59.0	58.7	-----
X.....	54.1	45.8	61.7	26	58.0	66.5	13
TCE.....	52.2	44.9	64.8	31	57.6	68.0	13
MC.....	51.5	44.4	56.3	21	55.1	64.0	15
T.....	54.3	45.7	55.3	17	57.0	68.0	10
Am Ac.....	53.6	39.7	52.3	24	56.7	66.2	16
EA.....	51.5	44.4	60.0	26	54.1	63.0	14
1A:1MC.....	51.2	42.5	58.0	27	57.2	59.1	14

The liquid composition used in the foregoing Table VI contains hexamethoxymethylmelamine but no chemical curing agent. As before, the opacity following the solvent treatment steps is increased relative to the light transmission in the treated area after the first and second water treatment steps. In every instance, the opacity of the treated area is increased after the first water treatment and following solvent treatment relative to the light transmission of the original paper. This is also true following the second water treatment and following solvent treatment step.

about one minute. The paper is then dipped in acetone and again dried in a similar manner.

Example 8

A liquid impregnating composition is employed using hydrogenated methyl ester of rosin (Hercules Chemical Co.) without an added solvent or a chemical curing agent. Two water treatments and an acetone treatment, similar to the process steps described in Example 1, are used to obtain an opaque area.

TABLE VI

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Solvent	Blank	First Water Treatment	Solvent Treatment	Percent Change 100×(2)−(3)/(3)	Second Water Treatment	Solvent Treatment	Percent Change 100×(5)−(6)/(6)
A.....	52.1	53.2	66.2	20	57.5	60.8	5
CT.....	55.3	52.0	67.0	22	62.7	69.5	10
H.....	55.0	55.8	63.5	12	61.7	66.8	8
X.....	54.6	53.4	68.7	22	61.4	68.8	11
EA.....	54.5	55.1	64.5	15	61.3	66.8	8
MC.....	52.6	52.8	66.0	20	56.1	58.3	4
T.....	52.1	53.7	68.0	21	56.9	63.0	10
Am Ac.....	52.9	51.4	60.7	15	60.0	67.8	12
Ac An.....	52.7	53.8	67.8	21	59.3	66.0	10
1EA:1H ₂ O.....	55.3	51.0	62.0	18	-----	-----	-----
1A:1CT.....	53.1	51.3	66.0	22	59.8	64.7	8
1A:3MC.....	52.9	50.0	56.8	12	60.3	62.2	3
1A:1MC.....	54.9	52.7	67.0	21	60.1	67.3	11
3A:1MC.....	54.7	48.9	64.3	24	59.1	64.7	9

When reference is made to the use of "water" in the water treatment step, it is intended that this term may be used interchangeably in an equivalent manner with "aqueous liquids." Such liquids may particularly include sizing solutions commonly used in the paper art, most of which are starch solutions such as chlorinated and ethylated starches. When a sizing solution is used, it is meant to refer to surface sizing rather than internal sizing. An advantage of using such sizing solutions is that paper may be simultaneously sized and opacified. In the following

Example 9

The following liquid compositions A and B are prepared as follows:

A

Ingredient:	Parts by weight
Epoxy resin, Dow 332	3
Curing agent, U.S. Borax 110	1
Methyl Carbitol	5

13
B

Epoxy resin, Epon 812 ----- 6
Curing agent, Epon H-3 ----- 3
Methyl Carbitol ----- 8

14

single solvent treatments following the corresponding water treatment or treatments. The points along the Y axis of the graph represents the difference between the opacity of the control on untreated paper strips and treated, whether water treatment alone or water followed by an acetone treatment. The X axis of all the figures is divided by the same number of units, but the unitary divisions of the Y axis is varied to better depict the different degrees of measurement.

TABLE VII

	9 lbs.		13 lbs.		20 lbs.		24 lbs.		28 lbs.		36 lbs.	
	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper
Control.....	53.8	1.9	68.1	2.8	82.5	4.5	87.5	5.4	85.8	5.2	91.6	7.0
1st Water.....	42.1	-----	63.3	-----	76.8	-----	83.6	-----	86.2	-----	88.7	-----
Acetone.....	67.7	2.0	74.5	3.1	86.3	5.3	90.3	6.4	89.0	5.8	94.0	8.9
3d Water.....	48.3	-----	70.1	-----	80.8	-----	87.6	-----	89.5	-----	92.6	-----
Acetone.....	67.3	1.9	82.5	3.2	89.3	5.3	93.0	6.4	91.0	6.1	94.2	8.4
6th Water.....	55.0	-----	72.0	-----	80.9	-----	88.8	-----	90.8	-----	92.8	-----
Acetone.....	72.7	2.1	84.0	3.2	90.5	5.2	93.7	6.7	92.8	6.2	94.7	7.9
9th Water.....	58.9	-----	73.1	-----	81.9	-----	88.8	-----	90.9	-----	92.3	-----
Acetone.....	76.8	2.1	84.3	3.1	91.7	5.4	93.7	6.6	92.3	6.0	96.0	8.8
12th Water.....	61.8	-----	74.7	-----	83.0	-----	88.7	-----	91.3	-----	93.3	-----
Acetone.....	76.7	2.1	85.0	3.3	92.0	5.4	94.3	6.6	93.0	6.2	95.6	8.6

TABLE VII A

	9 lbs.		13 lbs.		20 lbs.		24 lbs.		28 lbs.		36 lbs.	
	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper
Control.....	54.0	1.9	70.4	2.9	82.5	4.7	87.4	5.4	85.6	5.1	90.9	6.9
1st Water.....	62.5	-----	72.3	-----	84.1	-----	89.1	-----	87.6	-----	92.4	-----
Acetone.....	64.3	2.2	71.0	3.4	84.2	5.7	88.7	6.9	88.2	6.0	91.8	8.0
3d Water.....	57.8	-----	70.6	-----	80.8	-----	86.3	-----	87.7	-----	90.9	-----
Acetone.....	54.0	2.1	68.5	3.3	80.8	5.4	86.0	6.5	88.0	6.2	91.5	8.7
6th Water.....	57.6	-----	70.3	-----	81.3	-----	86.7	-----	88.0	-----	90.9	-----
Acetone.....	55.7	2.3	70.3	3.3	81.3	5.4	87.0	6.4	87.3	6.0	91.0	8.1
9th Water.....	57.7	-----	70.8	-----	81.2	-----	87.0	-----	88.0	-----	91.2	-----
Acetone.....	56.5	2.2	69.0	3.3	81.3	5.4	87.0	6.4	87.8	6.0	90.2	7.8
12th Water.....	58.7	-----	72.0	-----	82.0	-----	87.5	-----	88.8	-----	92.2	-----
Acetone.....	56.7	2.2	72.0	3.2	87.0	5.4	87.7	6.4	88.2	6.0	92.0	8.4

treatment. The procedure for the water and acetone treatments was generally that described in Example 5. Opacity measurements were made on control strips, on the water treated strips and on the acetone treated strips. Various paper weights were used from 13 lb. to 36 lb., each paper weight containing 25% cotton. All the treatments were made on strips of each paper weight. Caliper measurements were made with a TMI micrometer, model 549M, Testing Machines, Inc., Mineola Long Island, N.Y. The thickness of the strips, control and treated, were measured in mil units. Following Table VII lists the results obtained with liquid impregnating composition A, and Table VII A lists the results obtained with liquid impregnating composition B. The opacity and caliper measurements represent the average of three readings on spaced portions of each strip.

Foregoing Tables VII and VIIA show that the caliper of the acetone treated strips was increased over the controls at least 5%. In many instances the caliper increase was 10% or even higher.

The data of Table VII (composition A) is utilized in

TABLE VIII

	9 lbs.		13 lbs.		20 lbs.		24 lbs.		28 lbs.		36 lbs.	
	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper	Opacity	Caliper
Blank.....	54.1	1.9	69.0	2.9	82.5	4.5	87.3	5.5	85.6	5.2	91.0	6.9
1st Water.....	60.0	1.9	72.4	3.1	83.2	5.2	88.0	6.8	86.2	6.0	91.8	7.5
Solvent.....	63.2	2.0	75.5	3.1	86.2	5.0	90.0	6.2	88.0	5.5	93.5	7.5
3d Water.....	58.9	2.1	74.4	3.1	85.0	5.0	89.5	6.3	87.6	5.8	92.1	7.7
Solvent.....	63.0	2.0	74.9	3.1	86.5	5.1	90.2	6.2	88.0	5.8	92.0	8.7
6th Water.....	56.3	1.9	73.3	3.1	85.7	4.9	89.7	6.0	88.1	5.7	92.2	7.9
Solvent.....	59.0	2.0	74.5	3.1	86.0	5.1	89.5	6.0	88.0	5.8	93.0	8.1
9th Water.....	55.8	1.9	73.5	3.1	85.2	4.9	89.3	6.0	88.5	5.7	92.3	8.5
Solvent.....	59.6	2.1	73.5	3.2	85.0	4.9	89.0	6.1	89.0	5.8	94.0	7.7
12th Water.....	53.2	1.8	73.0	3.0	85.5	4.8	89.0	5.8	88.0	5.6	91.8	7.5
Solvent.....	56.0	2.0	74.0	3.0	86.0	4.9	90.0	6.0	89.5	5.7	93.0	8.3

FIGURES 1-6 of the drawing to graphically represent the difference in opacity following an organic solvent treatment. The data collected from 9 lb. to 36 lb. paper strips is, respectively, shown in FIGURES 1 to 6. The increase in opacity is represented as being directly proportional to the number of water treatments, and a still further increase in opacity is seen from the curve plotted by the

Example 10

A liquid impregnating composition is prepared from the following ingredients in the amounts listed.

Ingredient:	Parts by weight
Polyvinyl chloride (Marvinol) -----	½
tripropionin plasticizer -----	10

A number of paper strips are dipped in water, nipped, dried and then dipped in acetone according to the procedures described in Example 5. Some of the strips have only one water treatment before the organic solvent treatment, and others have three, six, nine and twelve successive water treatments. Paper strips of varying weight are given the same treatments, and the opacity and caliper readings are reported as averages of three readings on spaced portions of each strip. Such averages are listed in the following Table VIII.

The data of foregoing Table VIII shows that the opacity does not, for the most part, substantially change with water treatment in excess of one. The solvent treatments, in general, lead to a greater opacity increase.

Example 11

A variety of liquid impregnating compositions were prepared, and paper strips were dipped in each liquid composition. Different sets of strips were given a different number of water treatment steps—from one to twelve successive water treatments with intervening drying steps generally as described in Example 5. Each of the strips,

having various numbers of water treatment steps, are then given one or two successive acetone treatments generally as described in Example 5. The opacity of the strips was measured and reported as an average of three spaced

measurements on the same strip. The various formulations are identified in Table IX, and the supplier is indicated in parenthesis next to the ingredient. The recorded opacity measurements are presented in following Table X.

TABLE IX

No.	Impregnating Material	Solvent	Hardener
860....	Staybelite ester No. 3 (Hercules).....		
853....	5 parts Dresenol 142 (Hercules).....	5 parts Methyl Carbitol.....	
856....	5 parts Santolite MS 80% Solution (Monsanto).....	do.....	
854....	Monoplex S-73 (Rohm & Haas).....		
848....	5 parts Paraplex G-40 (Rohm & Haas).....	5 parts Triacetin (Armour).....	
858....	5 parts Eastman Polymer Plasticizer NP-10 (Eastman).....	5 parts Methyl Carbitol.....	
859....	5 parts Santolite MHP (Monsanto).....	do.....	
864....	Monomer X-970 (Rohm & Haas) Butylene Dimethacrylate.....		
865....	Dow Polyglycol P-400 (Dow).....		
872....	5 parts Acrylonitrile butadiene styrene, Cycolac (Marbon).....	5 parts MEK plus 20 parts Triacetin.....	
878....	5 parts Polyvinyl chloride, Marvinol (U.S. Rubber).....	10 parts Kodaflex Tripropionin (Eastman).....	
879....	5 parts Morester X-983 (Pfizer).....	10 parts Kodaflex Tripropionin.....	
911....	Methyl Carbitol (Union Carbide).....		
932....	Aersol OT (Amer. Cyanimid).....		
912....	Tripropionin (Eastman).....		
907....	N-Methyl 2 Pyrrolidone (Gen. Aniline).....		
908....	Stab-U-Cel (Upson Chem.).....		
910....	Diethylphthalate.....		
642....	6 parts Epon 812 (Shell).....	8 parts Methyl Carbitol.....	3 parts Epon curing agent H-3 (Shell).
641....	5 parts Dow 332 (Dow).....	4.5 parts Methyl Carbitol.....	1 part Epoxy curing agent 110 (U.S. Borax).
913....	Bursperse (Buckman Labs., Inc.).....		
914....	Dibutylphthalate.....		
915....	Lucast bean gum.....		
916....	Hercules P-16 (Union Carbide).....		
919....	Silicone L-5310 (Union Carbide).....		
920....	Silicone L-530 (Union Carbide).....		
927....	Neolyn 40 (Hercules).....		
880....	5 parts Epoxyl resin E-11 (Shell) epoxy acrylate.....	10 parts Methyl Carbitol.....	
882....	Dresinol S 1621 (Shell).....		
873....	1 part Alcohol soluble butyrate (Eastman).....	3 parts Tripropionin.....	
884....	3 parts Sucrose acetate isobutyrate (Eastman).....	10 parts Methyl Carbitol.....	
886....	Surfynol 485 (Aircro Chem.).....		
892....	400 Distearate (Glycol Chem.).....		
896....	5 parts Hexoplas PPA (ICI Organ.).....	5 parts Methyl Carbitol.....	
901....	5 parts 1,2 Cyclohexane dicarboxylic anhydride (Matheson, Coleman & Bell).....	do.....	
897....	5 parts Paraplex 656 (Rohm & Haas).....	do.....	
906....	GAFAC PE 510 (General Aniline), Phosphate ester of polyoxy ethylenated alkylphenol.....		
899....	Polyethylene glycol (Wyandotte).....		

TABLE X

	860	853	856	854	848	858	859	864	865	872	878	879	880	882
Blank	53.2	53.7	54.5	53.1	54.3	54.3	54.3	54.3	54.3	54.3	54.3	54.3	54.3	54.3
1st Water	23.0	49.7	40.8	19.5	26.8	24.7	19.4	42.4	32.8	45.1	29.8	32.0	42.9	36.2
1st Acetone	65.5	62.7	65.2	63.8	64.7	55.8	63.0	62.5	67.5	53.2	62.5	64.7	60.1	66.2
2d Acetone	64.3	64.0	66.0	64.7	67.0	57.7	65.0	66.0	67.5	54.5	65.3	64.0	60.7	67.2
2d Water	22.8	50.0	45.1	21.7	28.1	24.3	20.2	55.1	43.5	44.7	37.3	36.5	48.6	41.6
1st Acetone	65.3	62.2	67.7	57.3	65.7	67.8	57.7	63.7	71.0	47.8	69.4	67.4	70.3	66.3
2d Acetone	67.7	63.7	68.8	59.7	67.5	67.7	61.0	64.7	69.5	49.3	69.0	68.0	70.7	65.3
3d Water	23.0	50.3	48.1	22.5	31.4	30.8	22.1	55.5	50.2	45.0	49.2	42.0	51.9	46.3
1st Acetone	64.3	58.0	69.3	59.3	69.2	67.7	56.7	68.0	70.5	53.8	66.0	71.3	72.5	65.8
2d Acetone	65.7	60.0	69.0	62.7	69.2	68.3	59.5	66.3	70.8	54.3	65.0	72.3	72.0	66.3
4th Water	23.7	52.0	53.6	23.4	33.3	29.5	25.7	52.4	49.3	56.2	61.1	49.5	54.7	49.8
1st Acetone	64.0	61.0	67.0	59.3	70.7	68.5	64.5	64.0	72.8	52.5	66.0	72.3	74.0	70.0
2d Acetone	66.0	61.7	67.0	63.3	70.8	70.3	67.8	64.8	71.5	53.3	65.3	72.7	75.0	69.3
5th Water	22.7	52.7	53.0	24.7	36.0	30.2		55.5	54.5	46.0	62.2	50.7	55.0	52.8
1st Acetone	57.7	64.5	68.3	69.7	67.7	68.3		57.7	72.0	53.7	65.8	71.0	74.3	71.0
2d Acetone	61.0	64.3	68.7	69.7	70.0	70.3		61.3	72.8	54.3	66.0	71.2	74.3	72.0
	873	884	886	892	896	901	897	906	899	911	932	912		
Blank	54.8	54.2	54.3	53.8	56.1	54.6	55.5	54.6	54.8	54.9	55.4	54.2		
1st Water	25.6	28.7	57.6	42.7	31.0	58.0	37.0	41.2	20.5	55.8	59.8	28.6		
1st Acetone	65.0	59.0	67.0	67.5	66.3	69.0	65.7	61.7	65.7	58.0	61.7	66.7		
2d Acetone	65.8	59.3	67.0	68.3	67.7	60.3	66.0	64.7	64.7		60.8			
3d Water	40.1	32.8	58.3	49.8	38.1	57.5	40.7	50.0	23.1	56.6	60.6	47.4		
1st Acetone	68.1	70.7	62.5	70.8	72.8	56.3	71.0	65.0	72.5	57.3	61.5	70.2		
2d Acetone	70.7	71.7	62.0	71.7	73.0	55.7	71.0	66.2	72.0		62.7			
6th Water	54.3	37.5	57.6	57.1	45.3	55.7	40.8	51.8	33.1	55.9	60.8	64.0		
1st Acetone	70.3	73.0	56.7	75.2	76.7	54.5	73.3	61.7	73.0	57.2	60.0	72.5		
2d Acetone	70.7	72.7	55.7	75.3	76.7	53.5	73.8	63.0	77.3		61.7			
9th Water	54.9	40.8	59.1	58.6	47.4	53.1	41.7	52.7	38.2	56.0	61.8	61.5		
1st Acetone	67.0	73.7	60.3	72.8	75.3	51.7	75.3	67.0	79.5	59.7	61.7	66.7		
2d Acetone	65.5	72.3	59.7	73.2	75.7	52.0	75.5	69.2	79.5		62.7			
12th Water	53.0	43.3	58.7	64.0	52.8	57.6	39.8	63.5	40.1	55.8	61.7	56.8		
1st Acetone	62.2	76.0	59.2	70.7	77.5	57.3	74.8	67.0	80.3	56.5	61.8	57.0		
2d Acetone	62.7	75.5	58.2	70.3	77.3	56.7	74.3	67.3	80.0		62.7			
	907	908	910	642	641	913	914	915	916	919	920	927		
Blank	54.9	55.3	53.1	53.7	52.2	56.8	55.0	55.0	55.0	55.0	55.0	55.0		
1st Water	57.5	60.2	19.6	60.7	42.7	23.7	22.9	17.4	40.3	30.7	16.6	35.9		
1st Acetone	55.5	61.3	31.3	64.7		45.3	59.7	64.0	66.8	63.0	65.5	58.8		
2d Acetone			34.0	65.3		57.3	60.7	66.5	66.5	64.3	65.7	58.7		
3d Water	58.4	59.1	23.7	57.5	47.5	32.0	33.6	25.6	43.3	55.9	23.6	41.0		
1st Acetone	60.2	59.3	36.5	55.3		51.3	71.3	70.3	66.8	76.7	70.2	70.3		
2d Acetone			68.3	54.7		67.7	71.7	71.0	66.3	76.8	70.0	70.3		
6th Water	59.3	59.6	26.0	57.0	51.2	37.2	39.1	29.9	45.5	66.5	33.4	44.9		
1st Acetone	58.8	60.5	40.5	55.8		64.0	75.3	69.3	63.7	73.7	66.3	75.8		
2d Acetone			55.5	55.8		69.5	75.3	69.7	67.7	74.0	77.7	76.0		
9th Water	60.3	59.5	28.7	57.9	53.7	44.6	41.0	36.2	47.8	66.9	36.1	47.9		
1st Acetone	60.2	60.0	46.2	59.0		66.0	74.0	71.0	66.7	70.8	79.5	77.8		
2d Acetone			62.3	58.8		70.7	74.7	70.7	67.3	71.5	78.7	78.8		
12th Water	61.3	61.2	31.0	57.7	56.2	47.0	45.8	41.8	47.7	67.3	39.7	62.0		
1st Acetone	63.0	61.7	48.8	58.7		66.3	75.0	75.3	66.3	71.0	77.2	79.0		
2d Acetone			63.7	57.7		70.7	76.0	75.5	68.0	71.7	78.0	79.0		

The identities of materials supplied under the various trade designations are said to be as follows:

Staybelite ester #3	-----	A triethylene glycol ester of a hydrogenated rosin.	
Dresenol 142	-----	A partially decarboxylated pale rosin.	5
Santolites	-----	Aryl sulfonamide formaldehyde resins.	
Paraplex	-----	Linear polyesters of aliphatic dicarboxylic acids and glycols.	10
Polyglycol 400	-----	Polypropylene glycol plasticizer, MW 400.	
Monoplex-73	-----	A monomeric epoxide ester.	
Morester X-973	-----	A saturated polyester.	15
Eastman polymer plasticizer	-----	A polymer derived from neopentyl glycol.	
Hexaplas PPH	-----	Polypropylene adipate.	
Lucast bean gum	-----	Algaroba.	20
Silicones L-530 and L-5310	-----	Organo-silicone copolymers.	
Aerosol OT	-----	Diocetyl sodium sulfosuccinate.	25

The data in foregoing Table X shows that a second successive acetone treatment even further increases the opacity of the strips, although the increase is not so dramatic as the increase of the first acetone treatment over the water treatment or treatments.

Example 12

A liquid impregnating composition is prepared from the following ingredients and amounts stated.

Ingredients:	Parts by weight
Urea formaldehyde (Parez 613-American Cyanamid Co.)	5
Methyl Carbitol	5

The above liquid composition is used to prepare an opaque area by the process steps of Example 1, using two water treatment steps and an acetone treatment step.

The improved process of this invention which uses a solvent in one or more solvent treatment steps leads to a recognizable and measurable opacity. The perceptible opacity is recognized by visual observation and the measurable opacity is one in which the opaque area is raised at least about 5% relative to the original thickness of the paper and in which the opacity is increased at least 1% relative to the light transmission of the original paper. While the foregoing measurable indices are often attained with one water treatment step alone and nearly always with two or more water treatment steps, the development of the opacity is enhanced by employing one or more solvent treatment steps following such water treatment steps.

In many instances, the enhanced development of the opacified area is visually recognized in that the area appears more opaque and has a better definition relative to the balance of the paper which is not opacified. In any event, this enhanced development or opacity is readily confirmed by the opacity measurements described herein. The improved practice of the process requires that at least one organic solvent treatment step be employed following one or a plurality of water treatment steps and intervening drying steps in the treated area. Whether one or more than one organic solvent treatment steps are employed, the opacity is improved as confirmed by visual observation and opacity measurements. Some practitioners may be satisfied with the degree of opacity developed following a single series of steps which includes a water treatment, drying, a solvent treatment, and drying. Others may prefer to further enhance the development of such opacity by a successive series of such described steps. It is an advantage that the use of the solvent treatment steps can lead to the attainment of an opaque area of desired quality with an over-all fewer number of treat-

ment steps. The use of the solvent treatment step will, in most embodiments, lead to an opaque area having a quality which would otherwise be obtained only with additional water treatment steps alone.

What is claimed is:

1. A method for opacifying areas on paper which comprises applying a non-aqueous liquid composition to the surface of said paper, said composition including a resin capable of being laid down as a wet film, of impregnating the paper and of developing a plurality of opacifying interfaces when contacted with water, contacting said resin with water, drying said area to remove substantially all of the water, and contacting said area with an organic solvent to increase the opacity of said area.
2. A method as in claim 1 wherein the liquid composition is applied to a limited surface area of the paper in a selected design, said limited portion is then contacted with water and dried, and at least that limited portion is then contacted with said organic solvent to increase the opacity.
3. A method as in claim 1 in which the entire surface of the paper is contacted with the liquid composition, the entire sheet of paper is then contacted with said water and dried, and the entire sheet of paper is then contacted with said organic solvent.
4. A method as in claim 1 which includes the further steps of drying the area following contact with said water, repeating a successive number of water contacting and drying steps, and contacting said water treated area with said organic solvent, whereby said successive number of water contacting, drying and solvent treatment steps are executed in sufficient numbers to attain a desired degree of opacity of said area following said contact with said organic solvent.
5. A method as in claim 4 wherein a plurality of successive organic solvent and drying steps are executed to enhance the opacity of the treated area.
6. A method as in claim 1 in which the liquid composition includes an organic solvent in which the resin is soluble.
7. A method as in claim 1 wherein the liquid composition includes a curing agent for the resin, and said water contact step is effected before the deposited wet film cures into a hard film.
8. A method as in claim 1 in which the liquid composition includes a chemical curing agent for said resin.
9. A method as in claim 1 in which the liquid composition includes a thermosetting resin of the class of an epoxy, a polyester, a urea formaldehyde, a melamine formaldehyde, and hexamethoxymethylmelamine.
10. A method as in claim 9 in which the liquid composition is substantially free of a chemical curing agent for said thermosetting resins.
11. A method as in claim 9 in which the liquid composition includes a chemical curing agent for said thermosetting resin.
12. A method as in claim 1 in which the resin is of the class of a rosin, a substituted rosin, and a modified rosin.
13. A method as in claim 12 wherein the substituted rosin is a hydrogenated methyl ester rosin.
14. A method as in claim 12 wherein the modified rosin is a partially decarboxylated rosin.
15. A method as in claim 12 wherein the rosin is a

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substituted and modified triethylene glycol ester of hydro-
genated resin.

16. A method as in claim 1 in which the resin is an
ester of a polyol and a saturated diacid.

17. A method as in claim 1 wherein the resin is an
ester of a polyol and an unsaturated diacid.

18. A method as in claim 1 wherein the resin is a
dialkyl sulfosuccinate.

19. A method as in claim 1 wherein the resin is sucrose
acetate isobutyrate.

20. A method as in claim 1 wherein the resin is cyclo-
hexanone.

21. A method as in claim 1 wherein the resin is a
condensation product of cyclohexanone and methyl
cyclohexanone.

22. A method as in claim 1 wherein the resin is a
monomeric plasticizer, and said resin is used as a diluent
for an aryl sulfonamide.

23. A method as in claim 1 wherein the resin is a
polyalkylene glycol.

24. A method as in claim 23 wherein the resin is a
polypropylene glycol.

25. A method as in claim 1 wherein the resin is
acrylonitrile butadiene styrene.

26. A method as in claim 1 wherein the resin is an
alkyl ketene dimer.

27. A method as in claim 1 wherein the resin is a
polymeric plasticizer.

28. A method as in claim 1 in which the solvent is
of the class of a ketone, a halogenated hydrocarbon, an
aliphatic hydrocarbon, a hydrocarbon ether, an ester of
a monocarboxylic acid and an alkanol, a polyhydroxy
alcohol, an alkyl anhydride, an ester of an alcohol and a
dicarboxylic acid, and a cyclic hydrocarbon.

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29. A method as in claim 1 in which the liquid com-
position contains an organic solvent for said resin and
wherein

a substantial amount of the solvent in the deposited
liquid composition is removed prior to the first water
application step by a drying step,

the excess water is removed following said first water
application by a nipping step,

substantially all the water is then removed by a dry-
ing step,

the foregoing steps of water contacting and drying
are repeated a number of times sufficient to lead to
the desired opacity of the area,

then the dried paper is contacted with said organic
solvent,

the solvent is substantially removed to dry the paper,
and

the foregoing steps of organic solvent contacting and
drying are repeated a number of times sufficient to
attain the desired opacity of the area.

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