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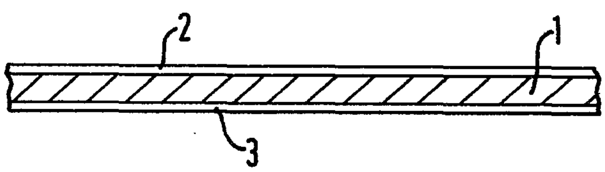
(54) **Improvements in dimensionally stabilized paper.**

(57) A method of improving the dimensional stability of a paper comprised at least in part of cellulosic fibres which includes covering both sides of the paper with a polymeric material and then polymerising the polymeric material by ionizing radiation or ultra violet light to form a hydrophobic coating.



EP 0 090 556 A1

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IMPROVEMENTS IN DIMENSIONALLY STABILIZED PAPER

This invention relates to paper having improved dimensional stability and to a process for the manufacture thereof.

Paper is conventionally made from cellulosic papermaking fibres by a progressive removal of water from an aqueous dispersion of the fibres until it develops its full strength as a finished paper when the moisture content is between about 4% and 8%. The final moisture content depends upon the kind of paper being manufactured and the operating conditions of the papermaking machine.

As the water content falls, water is withdrawn both from inter fibre and intra fibre spaces, with the consequence in the latter case, that the fibres shrink laterally but not longitudinally. At the same time, hydrogen bonds form at the points of interfibre contact so that the lateral fibre shrinkage causes longitudinal compression of the fibres to which they are bonded. As a whole therefore the paper web shrinks as it forms to a degree dependent upon the level of the hydrogen bonding which takes place within it.

The extent to which hydrogen bonding occurs is related to the physical characteristics of the cellulosic fibres used. Thus, wet or highly beaten fibres have their surface areas and suppleness increased as compared with less beaten fibres. This results in an increase in the degree of interfibre contact and thus also in the level of hydrogen bonding, with consequentially greater shrinkage of the web.

Because of the effect of moisture content on the level of hydrogen bonding and shrinkage, it will be apparent that, if the finished paper is subjected to conditions which produce alterations in the moisture content, this will affect the paper dimensions. Papers made from wet or highly beaten fibres, such as natural tracing paper, will of course be much more susceptible to dimensional changes as a result of alterations in moisture content, but most papers exhibit this undesirable phenomenon to at least a limited extent.

In this specification the term "natural tracing paper" is to be taken as referring to tracing paper in which transparency is conferred primarily by the pretreatment of the paper making fibres, and to distinguish from "prepared tracing paper" in which transparency is derived essentially from impregnants applied after the paper has been manufactured.

It is among the objects of the present invention to provide paper, having improved dimensional stability and a process for manufacturing such a paper. The invention has particular advantages for use with natural tracing paper but can be used effectively for the production of other papers in which improved dimensional stability is required.

According to the present invention a method of improving the dimensional stability of a paper comprised at least in part of cellulosic fibres which includes covering both sides of the paper with a polymeric material and then polymerizing the polymeric material by ionizing radiation or ultra violet light to form a hydrophobic coating.

The invention also includes a paper formed at least in part from cellulose fibres, each side of the paper having a covering of a polymeric material which has been polymerized by ionizing radiation or ultra violet light to form a hydrophobic coating, and a paper made according to the method set forth.

The use of materials polymerizable by ionizing radiation is particularly advantageous since such radiation has no direct effect on the moisture content of the paper. Other materials, in principle capable of providing dimensional stability, are normally only curable by processes involving the use of substantial heat, which reduces the moisture content unacceptably and affects the "lay-flat" characteristics of the paper.

The hydrophobic material may be a resin and may contain

a) in the case of natural tracing paper, a matting agent having substantially the same refractive index as the resin so as to enhance or at least not reduce the transparency of the paper. The matting agent may be incorporated in the resin applied to one or both sides of the paper, and served to compensate for any reduction in pencil or ink "take" resulting from the character of the cured resin.

b) opacifying agents, such as titanium dioxide.

c) flow modifiers and viscosity controllers. These include, for example, colloidal silica and various volatile solvents compatible with the resin being used.

d) functional additives such as polysiloxane to improve slip or release characteristics.

(e) inert fillers to a degree compatible with the maintenance of coating continuity.

(f) dyes and/or pigments to compensate for any undesired colour changes produced by the cured resin.

Treatment of the paper surface by corona discharge prior to coating with resin also serves both to facilitate resin flow and resin adhesion.

With papers such as natural tracing paper, made from wet beaten fibres, the paper will exhibit good holdout and the resin coating can be applied directly to the surface. In the case of paper having poor holdout (that is exhibiting a tendency to absorb liquid coatings applied thereto) pre-coats of polymers or copolymers, optionally containing filler materials such as clays or pigments, may be applied prior to application of the radiation curable material. Such precoats can be applied in either water or solvent media or as polymerizable resin.

The ionizing radiation used to cure the resin is preferably electron beam radiation which has the penetrative capability necessary to polymerise coatings on both sides of the paper sheet simultaneously. However ultra-violet radiation may also be used provided that a suitable photo-initiator is added to the resin coated onto the paper. But ultra-violet radiation can only be used for curing coatings on both sides simultaneously in the case of tracing paper or other papers which are transparent to such radiation. The invention also extends to the use of other forms of radiation such as gamma radiation, or radiation from Cobalt 60 or Caesium 137 sources, which can also provide the necessary energy to cure the resins.

The invention has been found to have particular advantages for use in the manufacture of a dimensionally stable tracing paper since it also enhances the paper transparency.

The invention will now be further described with reference to the accompanying drawings and Examples. Figures, 1, 2 and 3 are cross-sections through three different papers according to the invention, exaggerated in thickness for convenience of description.

Referring first to Figure 1, this shows a sheet of natural tracing paper 1 having coatings 2 and 3 on each side thereof each consisting of a film of hydrophobic polymer which has been polymerized from a previously applied coating by ionizing or ultra-violet radiation. One or both of the coatings 2 and 3 has dispersed therein a matting agent preferably having substantially the same refractive index as the polymeric film. One suitable matting agent is that sold under the trade name GASIL E.B.N. and manufactured by Crosfields, and is preferably present in the coatings at a concentration of between 10% and 15% of the coating by weight.

Figure 2 is a cross-section through another paper having good holdout and also carrying hydrophobic coatings cured by ionizing or ultra-violet radiation. In this case however the coatings 5 and 5 contain an opacifying pigment, for example titanium dioxide, to enhance the surface appearance of the paper. In the embodiment of Figure 3, a paper 7 having a poor holdout carries pre-coats 8 and 9 of polyvinyl alcohol over which hydrophobic coatings 10 and 11 cured by ionizing or ultra-violet radiation are provided.

In the embodiments of Figures 1 to 3, the coatings, 2, 3, 5, 6, 10 and 11 may be of various compositions suitable for cure by appropriate forms of ionizing or ultra-violet radiation.

Table I sets out twenty-six resin coating formulations, including diluents and matting agent, which perform satisfactorily in an electron-beam curing process, to provide an improved natural tracing paper of the kind described above with reference to Figure 1. Table 2 sets out the results from using various coatweights of the formulations of Table I in coating 70 grams per square metre natural tracing paper. Curing was carried out in a nitrogen atmosphere (less than 500 parts per million Oxygen) using an Otto Durr laboratory electron beam generating unit operating at 150 KeV (Kilo electron Volts). Wet expansion tests were carried out according to I.S.O. 5635/1978, a mean of three tests being taken for each example.

The results shown in Table 2 indicate that a substantial range of materials curable at varying dose levels by electron-beam curing provide a substantial improvement in both machine direction and cross-direction dimensional stability as compared with the uncoated paper.

The light transmission desnity values for the coated paper listed in the last column of Table 2 were derived in tests using a Baldwin Mk.5 Photometer. The results are taken from the scale readings on this instrument, the scale being zero to 2, zero representing a completely clear film and 2 a totally opaque substrate.

It will be seen from the transmission density values obtained, in comparison with the control, that the resin

T A B L E I

ELECTRON BEAM CURABLE FORMULATIONS

Two-sided Coating on 70 Gram per Sq. Metre Natural Tracing Paper

Formulation Number agent)	Resin as supplied by manufacturer % Oligomer		% Included Diluent	Added % Diluent	% Pigment (GASIL E.B.N matting agent)
1	54.6)			NONE	9
2	20.3)			60 HDDA	8
3	31.2)	Urethane HDDA	(17.8	41 TEGDA	10
4	31.2)	Acrylate	(17.8	42 TPDGA	9
5	19.1)		(10.9	61 TMPGA	9
6	23.5)		(13.5	54 NIBMA	9
7	51.0)			40 HDDA	9
8	43.0)			48 TEGDA	9
9	40.0)	Epoxy	NONE	51 TPGDA	9
10	27.0)			64 TMPTA	9
11	32.0)			59 NIBMA	9
12	61.0)			30 HDDA	9
13	49.0)	Acrylated		42 TEGDA	9
14	52.0)	Epoxidized	NONE	39 TMPTA	9
15	32.0)	Soya Bean		59 TMPTA	9
16	37.0)	Oil		54 NIBMA	9
17	40.8)		(27.2	23 HDDA	9
18	34.8)		(23.2	33 TEGDA	9
19	37.2)	Urethane	(24.8	29 TPGDA	9
20	27.0)	Acrylate	(18.0	46 TMPTA	9
21	31.2)		(20.8	39 NIBMA	9

TABLE I (Cont.)

Formu- lation Number agent)	Resin as supplied by manufacturer			Added % Diluent	% Pigment (GASIL E.B.N matting agent)
	% Oligomer		% Included Diluent		
22	79.0)			12 HDDA	9
23	73.0)	Polyester	NONE	18 TEGDA	9
24	73.0)	Acrylate		18 TPGDA	9
25	71.0)			20 TMPTA	9
26	73.0)			18 NIBMA	9

Note

1. Proportions calculated as percentages of total formulation

2. Diluent abbreviations :

HDDA - Hexane Diol Diacrylate
TEGDA - Tetraethylene Glycol Diacrylate
TPGDA - Tripropylene Glycol Diacrylate
TMPTA - Trimethylol Propane Triacrylate
NIBMA - N-(iso-butoxymethyl acrylamide)

TABLE 2

PROPERTIES OF 70 GRAMS PER SQUARE METER NATURAL TRACING PAPER WHEN COATED ON BOTH SIDES WITH ELECTRON BEAM CURED FORMULATIONS ACCORDING TO TABLE 1

Coating Formulation No. (From Table 1)		Radiation Dose per side (Kilo-Grays)	Coatweight per side (Grams per square metre	% improvement in resistance to wet expansion (I.S.O.5635/1978) compared to uncoated paper (control) Machine Direction	Cross Direction	Transmission Density (Baldwin
Control (uncoated paper)		---	-----	-----	-----	0.18
1		30	5.5	90	88	0.10
2	A	20	2.5	90	70	----
	B	30	2.5	70	75	0.11
	C	40	2.5	70	70	----
3		30	5.5	70	65	0.11
4		30	5.5	100	85	0.12
5	A	20	6.5	70	81	----
	B	30	7.5	90	93	0.11
	C	40	7.5	100	89	----
6		30	5.0	90	90	0.10
7	A	20	6.0	90	81	----
	B	30	5.5	70	93	0.11
	C	40	4.5	70	83	....
8		30	5.0	70	70	0.10
9		30	5.5	70	84	0.10
10	A	20	7.0	99	81	----
	B	30	5.0	70	89	0.10
	C	40	10.0	70	88	----
11		30	6.0	70	74	0.11

TABLE 2 (Cont.1)

PROPERTIES OF 70 GRAMS PER SQUARE METER NATURAL TRACING PAPER WHEN COATED ON BOTH SIDES WITH ELECTRON BEAM CURED FORMULATIONS ACCORDING TO TABLE 1

Coating Formulation No. (From Table 1)		Radiation Dose per side (Kilo-Grays)	Coatweight per side (Grams per square metre	% improvement in resistance to wet expansion (I.S.O.5635/1978) compared to uncoated paper (control) Machine Direction	Cross Direction	Transmission Density (Baldwin
12	A	20	5.0	60	79	----
	B	30	5.5	60	79	0.10
	C	40	6.0	100	80	----
13		30	4.5	80	63	0.12
14		30	5.0	70	84	0.11
15	A	20	6.5	90	78	----
	B	30	5.0	90	74	0.12
	C	40	6.0	100	78	----
16		30	4.5	90	70	0.10
17	A	20	6.0	90	70	----
	B	30	6.0	90	76	0.10
	C	40	6.0	100	90	----
18		30	7.0	100	80	0.10
19		30	7.0	100	94	0.10
20	A	20	6.5	90	90	----
	B	30	6.5	90	91	0.10
	C	40	6.5	90	93	----
21		30	5.0	100	73	0.10

TABLE 2 (Cont.2)

Coating Formulation No. (From Table 1)		Radiation Dose per side (Kilo-Grays)	Coatweight per side (Grams per square metre	% improvement in resistance to wet expansion (I.S.O.5635/1978) compared to uncoated paper (control) Machine Direction	Cross Direction	Transmission Density (Baldwin
22	A	20	5.5	50	55	----
	B	30	4.0	70	42	0.10
	C	40	5.5	50	70	----
23		30	5.5	90	76	0.12
24		30	5.0	50	53	0.10
25	A	20	6.0	70	80	----
	B	30	4.0	80	51	0.10
	C	40	5.5	80	78	----
26		30	6.0	100	76	0.10

coatings confer an increase in light transmission (and therefore transparency) on natural tracing paper.

The invention was also carried out using ultra-violet curable material. A formulation was prepared comprising 50% urethane acrylate, 33% Hexane Diol Diacraylate, 12% of a silica matting agent comprising GASIL E.B.N. (manufactured by Joseph Crosfield and Sons Ltd.) and 5% of a photo initiator 2-hydroxy-2 methyl-1 phenyl propan-1-one (DAROCUR 1173 manufactured by Merck.

Coating onto 70 gram per sq. metre natural tracing paper was undertaken using a screen printing squeegee in the laboratorey, variations in coatweight being achieved by varying the squeegee pressure. The coating was cured in the laboratory under a 200 watt per inch medium pressure mercury vapour lampa and a wet expansion test subsequently carried out using the I.S.O. 5635/1978 test.

The results are set out in Table No. 3, which shows that improvements in dimensional stability can be achieved using ultra-violet curable resins but that significant improvements can only be achieved at higher coatweights than in the case of electron-beam curable resins.

CLAIMS

1. A method of improving the dimensional stability of a paper comprised at least in part of cellulosic fibres which includes covering both sides of the paper with a polymeric material and then polymerising the polymeric material by ionizing radiation or ultra violet light to form a hydrophobic coating.

2. A method as claimed in claim 1 in which the polymeric material is a resin containing a matting agent having substantially the same refractive index as the resin.

3. A method as claimed in claim 1 in which the polymeric material is a resin containing an opacifying agent.

4. A method as claimed in claim 1 in which the opacifying agent is titanium oxide.

5. A method as claimed in claim 4 in which the resin contains a flow modifier.

6. A method as claimed in claim 5 in which the flow modifier is colloidal silica.

7. A method as claimed in claim 1 in which the polymeric material is a resin and contains an additive to improve slip or release characteristics.

8. A method as claimed in claim 7 in which the additive is polysiloxane.

9. A method as claimed in claim 1 in which the polymeric material is a resin and includes an inert filler to a degree compatible with the maintenance of coating

continuity.

10. A method as claimed in claim 1 in which the polymeric material is a resin and includes dye and/or pigments to compensate for any undesired colour changes produced by the polymerised resin.

11. A method as claimed in any one of the preceding claims in which the paper surfaces are treated by corona discharge prior to coating.

12. A method as claimed in any one of the preceding claims which includes applying a pre-coat of a polymer or copolymer prior to applying the polymeric material.

13. A method as claimed in claim 12 in which the precoating contains a filler material.

14. A method as claimed in claim 13 in which the filler material is a clay or pigment.

15. A method as claimed in claims 13 and 14 in which the pre-coat is a polymerizable resin.

16. A method as claimed in any one of the preceding claims in which the ionizing radiation is electron beam radiation.

17. A method as claimed in any one of the preceding claims 1-15 in which the ionizing radiation is taken from the group gamma radiation, radiation from cobalt 60, radiation from Caesium 137.

18. A method as claimed in claim 1 in which the polymeric material is one of those set forth in accompanying Table I.

19. A method of improving the dimensional stability of a paper web by the method described herein and with reference to and as shown in Figure 1, Figure 2 or Figure 3 of the accompanying drawings and in conjunction with accompanying Tables 1, 2 and 3.

20. A paper formed at least in part from cellulose fibres, each side of the paper having a covering of a polymeric material which has been polymerized by ionizing radiation or ultra violet light to form a hydrophobic coating.

21. A paper as claimed in claim 20 made according to the method set forth above in any one of preceding claims 1-19.

22. A paper formed at least in part from cellulosic fibres and provided with a hydrophobic coating substantially as described herein with reference to and as shown in Figure 1, Figure 2 or Figure 3 of the accompanying drawings.

FIG. 1.

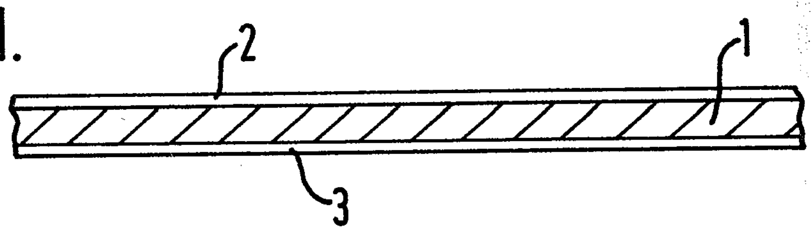


FIG. 2.

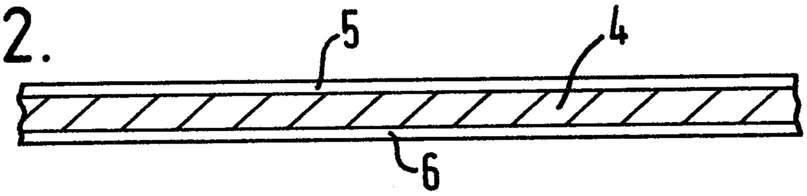
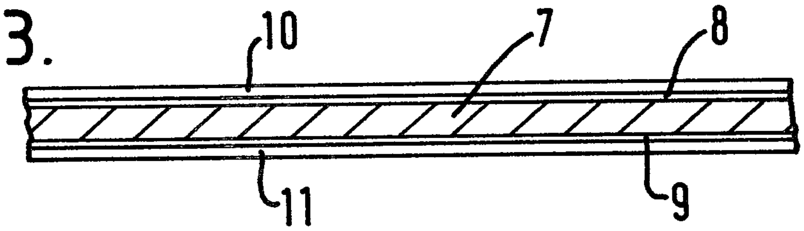


FIG. 3.



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EUROPEAN SEARCH REPORT

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Application number

EP 83 30 1502

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X,Y	US-A-4 246 315 (O. KOPP et al.) * Whole document *	1,15, 16,18-22	D 21 H 5/00 D 21 H 1/22 D 21 H 1/34

Y	GB-A-1 175 623 (IMPERIAL CHEMICAL INDUSTRIES) * Page 1, lines 12-60; page 2, lines 41-88 *	1,3,5, 6,19-22	

Y	MC-A-18 760 172 (P. GIRARD) * Whole document *	1,12-14,19-22	
	---		**TECHNICAL FIELDS SEARCHED (Int. Cl. 3)**
Y	US-A-4 137 046 (T. KOIKE et al.) * Column 1; column 2, lines 1-41; column 3, lines 10-35 *	1,18-22	
	---		D 21 H
Y	US-A-4 128 437 (S. URA et al.) * Column 1; column 2, lines 1-11; column 7, lines 37-65 *	1,5,18-22	
	--- -/-		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-06-1983	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 51, no. 7, January 1981, page 777, no. 7198, Appleton, Wisconsin, USA & JP - A - 80 67097 (BRIDGESTONE TIRE CO., LTD.) 20-05-1980 * Whole abstract *	1,18-22	
Y	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 47, no. 3, September 1976, page 334, no. 3201, Appleton, Wisconsin, USA & JP - A - 74 72408 (SANYO-KOKUSAKU PULP CO., LTD.) 12-07-1974 * Whole abstract *	1,16, 18-22	
Y	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 47, no. 2, August 1976, page 231, no. 2159, Appleton, Wisconsin, USA & JP - A - 74 72407 (SANYO-KOKUSAKU PULP CO., LTD.)12-07-1974 * Whole abstract *	1,18-22	TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
Y	DE-B-1 282 437 (H.A. SCHOELLER SÖHNE) * Whole document *	1,18, 19,21	
Y	GB-A-2 066 732 (AZONA) * Frontpage *	1	

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THE HAGUE	17-06-1983	NESTBY K.

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0090556
Application number

EP 83 30 1502

Page 3

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 52, no. 4, October 1981, page 474, no. 4333, Appleton, Wisconsin, USA & JP - A - 80 29200 (MITSUBISHI PAPER MILLS LTD.) 01-08-1980 * Whole abstract *	1,3,6, 12,19-22	
A	GB-A- 213 810 (R.W. BRUMBY et al.) * Page 2 *	1,10, 19-22	
A	US-A-4 177 314 (R.W. STEEVES) * Whole document *	1,16, 18-22	

TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

The present search report has been drawn up for all claims

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