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STIFF, STRONG PAPER

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The present invention relates to waterlaid cellulosic webs of improved stiffness. More particularly, the present invention relates to stiff, non-elastic cellulose webs composed of cellulose fibers carrying polymerized methyl methacrylate.

At present, stiff cellulose webs are made by impregnating a preformed paper web with an aqueous solution of a stiffening agent for example sodium silicate, glue, or gelatin followed by drying. Thick webs (for example carboard) are formed by laminating two or more comparatively thin webs containing a stiffening agent, an adhesive being used when necessary to unite the plies.

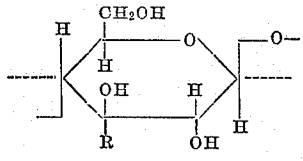
Webs of this type are used in the manufacture of filing cards, punched cards, playing cads, tags and cardboard (including Bristol board). For brevity, these webs are hereinafter generically termed "stiff paper."

Stiff paper produced by the foregoing processes is of limited utility, one reason being that its stiffness is rapidly destroyed by water. The paper usually becomes limp after a few moments of soaking in water, and its stiffness often changes markedly in humid weather. A further disadvantage is that the paper tends to crack quite easily.

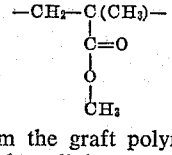
Stiff paper has also been prepared by use of a water-soluble thermosetting resin. The paper is impregnated with an aqueous solution of the resin and is then dried at elevated temperature for a time sufficiently long to thermoset the resin. The resin, however, tends to form a continuous phase in the paper so that the porous open structure of the paper and its writing properties are changed and the paper becomes brittle. Moreover, the resin in such paper is not chemically attached to the fibers by carbon-to-carbon linkages and thus is subject to removal by the action of acid or alkali.

The discovery has now been made that paper composed of waterlaid papermaking fibers of cellulose carrying polymerized methyl methacrylate chemically reacted therewith possesses improved stiffness. We have found that such paper, when carrying preferred amounts of the polymer, is suitable for the purposes described above.

The reacted cellulose molecules have the theoretical formula



or an isomer thereof, wherein R is a vinyl chain principally composed of



units resulting from the graft polymerization of methyl methacrylate with the cellulose.

Paper carrying equal amounts of methyl acrylate in place of methyl methacrylate is distinctly different, being flexible and elastic.

The development of stiffness in paper of the present invention becomes apparent when the paper contains about

20%–25% by weight of the polymer and in that range the paper is distinctly stiffer than corresponding paper containing none of the polymer. At about 150% polymer content by weight the paper is about as stiff as normal filing or index card stock. At about 250%–300% polymer content the paper has nearly the stiffness of celluloid sheeting of the same caliper, and about the same springiness and snap. In practice we have found that paper containing 50% to 150% polymer by weight is generally suitable for the purposes set forth and this range is consequently preferred as affording a desirable product which has a desirably high stiffness and springiness without brittleness while minimizing consumption of the polymer.

The paper of the present invention has the open porous structure characteristic of ordinary paper and resembles it in color, texture and appearance. Its surface is inherently sized so that it has satisfactory resistance to water, ink and lactic acid. It has a good writing surface.

The paper of the present invention is highly resistant to the effects of acids and alkalis, and furthermore is highly resistant to the action of ultraviolet light. It is not susceptible to attack by microorganisms which destroy or damage normal paper. For these reasons and because of its stiffness at even low calipers it is suited for fabrication into shingles used in covering the roofs and sides of residences and industrial buildings.

Paper of the present invention may be prepared by impregnating a waterlaid cellulose web with an aqueous solution of a free radical initiator thereby activating the paper for graft polymerization and then contacting the paper, while thus activated, with a fluid emulsion of methyl methacrylate.

We find it most convenient to prepare an aqueous emulsion of methyl methacrylate and add to the emulsion an initiator such as ceric ammonium sulfate, ceric ammonium nitrate or cobaltic sulfate. The residence time of the paper in the emulsion varies at room temperature from a few minutes to an hour depending upon the amount of methyl methacrylate which it is desired to incorporate; the reaction time is decreased by moderate increases in temperature.

The present invention includes paper having a reacted content of other polymers. Thus the paper may contain a small amount of acrylonitrile to improve abrasion resistance and dimensional stability, methyl acrylate, ethyl acrylate, as diluents, and vinyl chloride and vinylidene chloride to decrease flammability. Minor amounts of these materials, up to about 15% of the weight of methyl methacrylate present, are tolerated but in general do not act to improve the stiffness of the paper and usually produce an opposite effect.

The stiffness of the product evidently results from the entangling effect or the interlacing of the developed polymer chains; the reason why the paper of the present invention is so stiff compared with paper made from ethyl acrylate or methyl acrylate may be due to the inherent stiffness of the methacrylate chain compared with the acrylate chain, but we do not wish to be limited to any theory.

The invention will be further described with reference to the examples which follow. These examples constitute specific embodiments of the invention and are not to be construed as limitations thereon.

Example I

The following illustrates the preparation of card stock according to the present invention showing the stiffness imparted by low, intermediate and high amounts of methyl methacrylate.

A stock emulsion was prepared by emulsifying 6.5 parts by weight of monomeric methyl methacrylate in

100 parts by weight of water containing 0.05% by weight of dimethyl octadecyl benzyl ammonium chloride in water at room temperature. The emulsion was purged of air by the use of nitrogen.

To prepare each paper sample, an amount of the emulsion containing several times the weight of methyl methacrylate to be reacted were run into a closed treating vessel containing paper (a saturating sulfite-α pulp stock having a basis weight of 10 lbs./1,000 ft.^{2}) supported on a stainless steel rod; ceric ammonium sulfate catalyst solution was run in with gentle agitation in such amount as to make the emulsion 0.005 molar in ceric ion, the pH reduced below 2 by addition of nitric acid, and the contents of the vessel gently agitated.

The polymer content of the paper was determined by weighing each sheet before and after treatment. The stiffness of each sheet was determined after drying by the Gurley tester [Paper Trade J. 110, No. 7:29 (Feb. 15, 1940)]. The springiness of the sheets was determined by snapping a corner of the material with the finger, and the writing properties of the material were determined by the use of fountain pen ink.

No.	Methyl Methacrylate Content, Percent	Stiffness, mgm.	Remarks
A	None	49.0	Limp. Very absorbent. No sizing.
1	56	90.6	Definite snap. Good writing surface.
2	100	242.0	Good snap. No elasticity.
3	193	317.0	Very good snap.
4	280	594.0	Strong spring and snap. No elasticity, not brittle. Hard surface. Good writing properties.

Extraction of samples of the sheets with water, ethyl acetate, benzene and carbon tetrachloride caused no noticeable change to the sheet material.

Repetition of the foregoing paper treatment using methyl acrylate in place of methyl methacrylate yielded a limp product having a suppleness similar to that of chamois leather.

We claim:

1. A web composed of waterlaid papermaking cellulose fibers uniformly carrying on at least the surface thereof between 25% and 300%, based on weight of said fibers, of polymerized methyl methacrylate, said polymerized methyl methacrylate being directly graft polymerized to said cellulose.

2. A web according to claim 1 wherein the weight of polymerized methyl methacrylate is between 50% and 150% of the weight of the cellulose.

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