A Water-Soluble Hydantoin Epoxide/ Polyamine System as a Wet-Strength Additive for Paper

INTRODUCTION

The usefulness of wet-strength paper is fairly obvious and lies in any application where paper can come into contact with water (e.g., maps, wrapping paper, etc.). Wet-strength paper is defined according to the *Dictionary of Paper*[1] as "paper which has extraordinary resistance to rupture or disintegration when saturated with water—this property being imparted by chemical treatment of the paper or of the fibers from which it is made." Wet-strength paper is characterized by the residual tensile strength of the paper after wetting, expressed as a percentage.[2] Normal untreated paper made from cellulosic fibers retains only 3–10% of the original dry tensile strength when saturated with water,[2] and it has been suggested that papers possessing a wet tensile strength of more than 15% of the dry tensile be considered wet-strength papers.[3]

A very large number of polymer systems have been investigated as wet-strength additives, and it is quite common to achieve wet strengths of 20–40%, exceptionally 50%, of the dry strength. Polymer systems which are substantive to cellulose may be added directly to the pulp before the paper has been formed (beater addition); other systems can be applied by impregnation of the finished paper.

Schroeder[4] has investigated the use of epoxy resin–curing agent formulations as wet-strength additives for paper; he obtained wet tensile strengths of approximately 36% with an add-on of approximately 2% for a glycerin polyepoxide–zinc fluoroborate combination applied to finished paper, via impregnation, as a water-based emulsion.

With the advent of completely water-soluble hydantoine epoxy resins, we felt that it would be of interest to investigate this type of resin as wet-strength additive. We are reporting results obtained with a water-soluble hydantoin bisepoxide resin–aliphatic polyamine formulation and particularly the results of a 2^3 full factorial experiment carried out to determine the effect of chosen variables on wet strength.

EXPERIMENTAL

Materials

The hydantoine epoxy resin used in this study consisted of a 70/30 mixture of *N,N*-diglycidylhydantoin[5–7] and *N*-glycidyl-*N'*-glycidyloxypropyl-5,5-Dimethylhydantoin.[8–11] It had an epoxide equivalent weight of 144.

N,N-Dimethylaminopropylamine and Tris-dimethylaminomethylphenol (DMP-30) were used as supplied by CIBA-GEIGY & Co., Basle, Switzerland (technical grade); Triton X-100, a nonionic surface-active agent, as supplied by Röhm and Haas. The paper used was Whatman Quality 3 MM obtained from Whatman & Co., England.

Preparation of Wet-Strength Composition

N,N-Dimethylaminopropylamine was used at the catalytic concentration of 13.8 phr with the hydantoin epoxide. The two components were dissolved in water at room temperature and the ensuing solution then diluted appropriately (see below).

Application of Hydantoin/Polyamine Formulation

The hydantoin system was applied by impregnation, the impregnation being carried out in an impregnating tray with nip rolls. The optimal distance between the nip rolls with regard to the criteria of (1) best possible paper transport and (2) even distribution without subsequent dripping was determined in a series of preliminary experiments with water as the impregant. These experiments showed that a distance between rolls of 1–1.5 mm corresponded to a water pickup of 100–110%.

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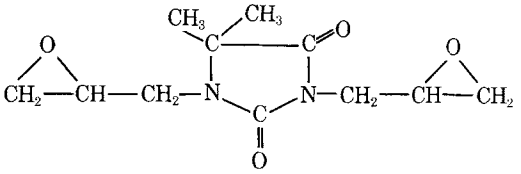
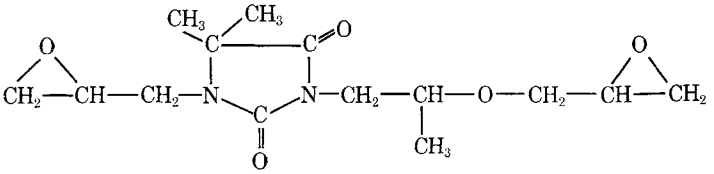
The water pickup was determined by weighing immediately after impregnation. The distance between the nip rolls was then fixed at 1.5 mm in order to give a wet pickup of 110%. The reproducibility was tested by impregnating samples of different dimensions and subsequent determination of the wet pickup. An error margin of ±2% was found. In the course of subsequent work, the wet pickup was checked repeatedly and found to remain constant at 110 ± 2%. By using impregnating solutions with a solids content of 0.91%, ultimate add-ons of 0.98–1.02% were thus obtained. Two to three drops (≤1%) of a nonionic surface active agent, Triton X-100, were added to the impregnating solutions. All samples were predried at room temperature for 30 min followed by a postcure at 130°C. The postcure at 130°C is intended to simulate industrial conditions, as wet-strength additives usually cure within a few weeks at normal temperatures after application to the paper. Assuming that the reaction rate doubles every 10°C, 10 days of cure at room temperature can be shown to be very approximately equivalent to 7 min of cure at 130°C.

Tensile Strength Measurements

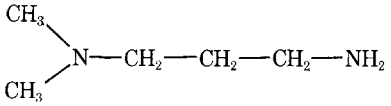
The tensile strength was determined on an Amsler Horizontal Tear Machine at a speed of 50 mm/min and converted into a "breaking length" in meters. The breaking length is the length of a (hypothetical) strip of paper which would tear under its own weight. Ten 140 × 15 mm samples were tested in each case. The wet-strength measurements were carried out on samples which had been immersed in water for 60 min. Surplus water was removed by very short contact with filter paper, and the samples were then immediately tested. The Whatman Quality 3 MM paper used in this work had an initial dry tensile length of 1605 m (±2%).



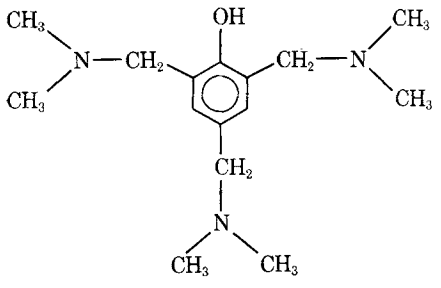
N,N-diglycidyl-5,5-dimethylhydantoin



N-glycidyl-*N'*-glycidyloxypropyl-5,5-dimethylhydantoin



N,N-dimethylaminopropylamine



tris-dimethylaminomethylphenole (DMP-30)

RESULTS AND DISCUSSION

Effect of Epoxy/Amine Ratio

It is standard practice in epoxy technology to use *N*,*N*-dimethylaminopropylamine at an amine hydrogen to epoxy ratio of considerably less than 1:1, the assumption being that crosslinking also takes place via the tertiary amino group. The same procedure was adopted with the new hydantoin epoxy resin, and first results were obtained with an epoxide/amine weight ratio of 100:13.8.

Table I shows the effect of a variation of ±20% on the wet and dry strength of the paper tested. The table shows wet strength retentions of the order of 50%, which was judged to be encouraging and which led us to carry out further experiments as outlined below. The hydantoin–epoxy system also leads to an improvement in dry strength of approximately 20%. This secondary positive effect is not self-evident, as many wet-strength polymers do not automatically also lead to an improvement in dry strength. The very large class of aminoplast wet-strength resins, for example, may produce a considerable improvement in wet strength with very little change in other physical properties[2] (e.g., dry strength). The improvements in wet and dry strength brought about by the new hydantoin system are sensitive to a reduction, but not apparently to an increase, in the amount of polyamine (±20%).

Factorial Experiment

The rudimentary check on the epoxide/amine ratio described above showed the initially chosen amine concentration of 13.8 phr to be substantially correct. This ratio remained unchanged for the following factorial experiment in which the influence of three further parameters on wet-strength performance was investigated:

Factors	Levels	
	(−)	(+)
A: reactivity → accelerator DMP-30	0%	5%
B: age of the impregnating solution	0 days	7 days
C: concentration of the impregnating solution	0.5%	1%

A 2^3 full factorial design was used, i.e., eight experiments were carried out. The experimental design and results are given in Table II.

The average effects were determined according to the Yates method[12] and are listed in Table III.

The significance was determined graphically using a half-normal plot.[13] The null hypothesis states that all the measured effects are part of a normal population and therefore normally distributed. Large effects that apparently deviate from normality are considered to be significant. In practice,

TABLE I
Wet and Dry Strength as a Function of Epoxy/Amine Ratio[a]

Amine, phr	Wet Strength after 60 min immersion, m	Wet strength/ dry strength ratio, %[b]	Dry strength after treatment, m	Dry strength improvement, %
11	I 601	37.4	1680	+4.7
	II 684	42.6	1747	+8.8
13,8	I 793	49.4	1900	+18.4
	II 863	53.8	1904	+18.6
16,6	I 811	50.5	1899	+18.3
	II 836	52.1	1918	+19.5

[a] Initial dry strength of untreated paper: 1605 m. All tensile strengths converted to breaking lengths; add-on 1 ± 0.02%; drying conditions I: 30 min at room temperature + 30 min at 130°C; II: 30 min at room temperature + 60 min at 130°C.

[b] Based on the initial dry strength of the untreated paper.

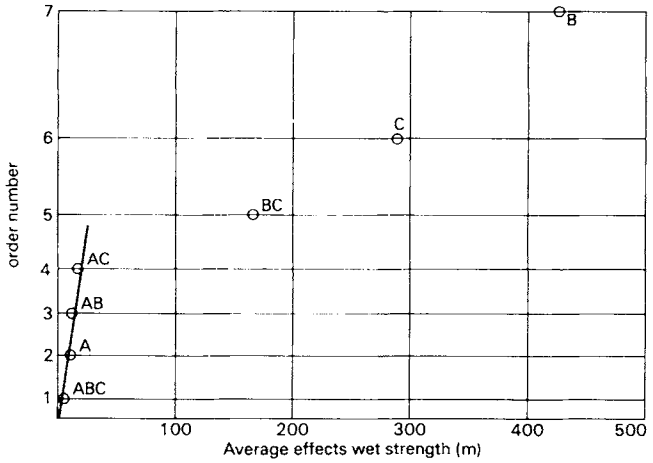


Fig. 1. Half-normal plot of order number vs. average (absolute) effects wet strength.

the effects are plotted in ascending order on a half-normal diagram. A straight line is then drawn through the appropriate effects so as to give a best possible fit—this line should be drawn by eye (and not, for instance, by using linear regression). The large effects which are not on or "near" this straight line are considered to be significant. This graphic method is not only time saving and convenient but has the added advantage of not being arbitrary. (The statistically significant effects of a factorial experiment are usually determined by arbitrarily designating higher-order effects as the experimental error and using this estimate to test the significance of the other, lower-order, effects.) A further advantage of the graphic procedure is that it offers a quick method of estimating the standard error of the experiment.

Figure 1 shows the effects of the factorial experiment plotted on an appropriate half-normal di-

TABLE II

Factorial Experiment: Hydantoin Bisepoxide/*N*,*N*-Dimethylaminopropylamine 100:13.8. Influence of Reactivity (Factor A), Age of Impregnating Solution (Factor B), and Concentration of Impregnating Solution (Factor C) on Wet Tensile Strength

Factorial design				Results	
Expt.	Factors			Wet strength after 60 min	Wet Strength/ Dry Strength
No.	A	B	C	immersion, m[a]	ratio (%)[b]
1	−	−	−	345	21.5
2	−	+	−	90	5.6
3	−	+	+	235	14.6
4	+	−	+	820	51.1
5	+	+	+	210	13.1
6	+	−	−	380	23.7
7	+	+	−	110	6.9
8	−	−	+	810	50.5

[a] All tensile strengths converted to breaking lengths in m.

[b] Based on the initial dry strength of the untreated paper (= 1605 m). Drying conditions: 30 min at room temperature + 30 min at 130°C.

TABLE III

Measured property (response)	Effects						
	A	B	AB	C	AC	BC	ABC
Wet strength after 60 min of immersion in water	10	−427.5	−12.5	287.5	−17.5	−165	−5

agram. The effects AC, AB, A, and ABC can easily be represented by a straight line. The effects BC, C, and B are clearly not on this straight line and are therefore (highly) significant. The fact that the straight line goes through the origin indicates that the experimental results may be treated in this way.

Finally, the standard error of the experiment can be estimated from the (remaining) four effects AC, AB, A, and ABC by determining the effect which corresponds to the order number closest to 68.5%. This order number is 3 ($\frac{3}{4} \times 100 = 75\%$), and the corresponding effect is AB with a numerical value of 12.5 m. (This estimate could then be used for an F-test; or, alternatively, the effects AC, AB, A, and ABC could be pooled and used as an error estimate. However, in view of the fact that the effects B, C, and BC are obviously highly significant, these supplementary tests were not deemed necessary.)

Of the three factors investigated in the factorial experiment, two have thus been shown to have a very marked effect on wet strength: The use of a seven-day-old impregnating solution of the hydantoin bisepoxide/polyamine formulation instead of a freshly prepared solution leads to a considerable reduction in wet-strength retention, whereas this property is raised when the concentration of the impregnating solution is doubled, from 0.5 to 1%. The negative effect due to aging is far greater than the positive concentration effect, as can be seen from a comparison of the numerical values, −427.5 and 287 m, respectively.

As might be expected, this is reflected in the fact that when both factors are changed simultaneously, i.e., age of the impregnating solution from 0 to 7 days and concentration of the impregnating solution from 0.5 to 1%, the negative effect predominates and a negative interaction with a numerical value of −165 m results.

The very strong negative effect due to aging might be explained by assuming that effective impregnation/crosslinking does not take place after a certain critical molecular weight has been reached. A higher molecular weight could mean less penetration and less intimate association with the cellulose fibers. During cure there would be less *in situ* crosslinking and therefore possibly less resistance to swelling. Conversely, by doubling the amount of low-molecular-weight additive, one might expect an increase in wet strength retention because of higher concentration of crosslinked sites within the fiber structure.

In view of the preceding discussion, the acceleration of the hydantoin epoxide/polyamine reaction might have been expected to affect wet-strength retention. Depending on whether the acceleration was more effective before or after impregnation both a negative and a positive effect could have been imagined. As has been seen, however, the addition of a substantial amount of accelerator to the basic hydantoin/polyamine formulation has shown absolutely no effect on wet strength properties.

Industrial Considerations

The hydantoin bisepoxide/polyamine system we have described is noncationic and therefore nonsubstantive to paper fiber so that application via the impregnation procedure was investigated first. Noncationic wet-strength additives offer several advantages: they cause no problems with fluorescent whitening agents, anionic dyestuffs, or anionic debris. The first-generation urea and melamine/formaldehyde paper resins require acidic conditions for cure; this is mainly achieved by the addition of alum which can give rise to ecological problems and was one of the prime reasons for the development of the newer-generation polyamide/epichlorohydrin resins, which do not require acidic conditions for cure.[14] The latter are supplied as approximately 10–20% solutions in water. A two-component epoxy/curing agent system might offer an advantage here as both components can be stored and shipped as 100% solids.

A major disadvantage of the hydantoin–polyamine formulation described in this paper is that wet-strength performance appears to be very strongly influenced by molecular weight. The system would have to be used rapidly after initial mixing of the two components. Future work should be aimed at eliminating this disadvantage.

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