Dialdehyde Starch in Paper Coatings Containing Soy Flour-Isolated Soy Protein Adhesive

By F. B. Weakley, M. E. Carr and C. L. Mehltretter, Peoria, Illinois (USA)

A combination of soy flour and isolated soy protein was investigated as the adhesive in pigmented paper coatings that contained dialdehyde starch (DAS) as the insolubilizing agent. A coating formula of 50% solids made up of 8.3 parts soy flour, 8 parts isolated soy protein and 0.5 part DAS per 100 parts of clay exhibited pseudoplastic and thixotropic flow properties characteristic of coating colors containing more costly protein adhesives. Both wax pick and wet-rub resistance of the paper coating were improved and putrefaction retarded by the use of DAS in the formulation. Brightness, wax pick and wet-rub resistance values compared favorably with those of a reference coating containing 12.5 parts of isolated soy protein and 0.5 part DAS per 100 parts of clay.

(Zusammenfassung siehe Seite 194; Résumé à la page 194)

Introduction

Insolubilization of casein binder by crosslinking with dialdehyde starch (DAS), to impart a high degree of wet-rub resistance to pigmented paper coatings, was described in a previous study [1]. Past price instability of casein, however, prompted an investigation of other commercially available proteins, which could be crosslinked with DAS, for use as adhesives to provide wet-rub resistant coatings for paper.

Soy flour is compatible with various proteins and has been an effective extender for isolated soy protein used in coating and printing wallpaper [2]. In our latest work, pigmented paper coatings containing an approximately equal weight of soy flour and isolated soy protein, both with and without DAS as the insolubilizing agent, were compared with reference coatings that contained isolated soy protein as the pigment binder on an equivalent protein basis. Rheological properties, wax pick resistance and wet-rub resistance were evaluated.
Experimental

Coating Color Preparation

A reference coating color containing medium-viscosity isolated soy protein as the sole adhesive was formulated as shown in Table 1. Adhesive dispersion was prepared by coating pigment from J. M. Huber Corp., New York, New York. pH 7.2 and adjusted to 82.2 parts with fiber, hand-rubbed DAS (Sumstar-190l), Miles Laboratories, Inc., Stoughton, Massachusetts) and with a Ferranti-Shirley Cone and Plate viscometer (Ferranti Electric, Inc., Electronics Division, Plainview, L.I., New York) and 1 and 24 h after completion of each formulation.

Rheograms of the coating colors, with and without DAS premix, were made at 27°C.

Coating Color Application

The coating colors were applied to magazine-grade raw stock of 70 gsm basis weight. Drawdown coatings were made with a Bird film applicator and averaged approximately 14 gsm (10 lb/ream, 25 × 40 = 500). The coated hand-sheets were dried at 135°C for 1 min in a forced-draft oven, and then conditioned at 23°C and 50% RH for 24 h before testing.

Testing

Wet-rub resistance: Wet-rub resistance was evaluated by a finger test, developed and described in previous work [1], with ratings of poor, fair, good, very good and excellent. A rating of excellent meant that there was no visible sign of coating removal and is typical of label-grade coatings. A rating of poor is typical of noninsolubilized starch-coated papers ordinarily used for letterpress but which are unsatisfactory for offset printing.

Wax pick: Critical wax strength number of the paper coating was obtained by the basic wax pick test method, T 459 su-65.

Brightness: Brightness of coated hand sheets (oven-dried) was determined in a Hunter reflectometer.

Results and Discussion

The reference coating color formula contained 12.5 parts of isolated soy protein, 0.5 parts DAS and 100 parts of clay (Table 1). By substituting 8.3 parts of soy flour (4.5 parts protein basis) for 4.5 parts of the isolated soy protein in the reference formula, the time required to achieve a smooth, uniform mix was shortened. The quantity of aqueous am-

Table 1. Formulas for Reference and Experimental Coating Colors.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Reference coating color</th>
<th>Experimental coating color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating pigment</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Sodium hexametaphosphate</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Isolated soy protein,</td>
<td>12.5</td>
<td>8</td>
</tr>
<tr>
<td>Defatted soy flour, 200-mesh</td>
<td>0.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Aqueous ammonia, 28% concent.,</td>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>DAS® premix, 10% concent.</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Total solids, 50% pH 7.2</td>
<td></td>
<td>Total solids, 50% pH 6.9</td>
</tr>
</tbody>
</table>

a) Hydrasperse from J. M. Huber Corp., New York, New York. Physical form: pulverized; b) Delta protein in the medium viscosity grade, Central Soya, Chemurgy Division, Chicago, Illinois; c) Prosoy L, Central Soya, Chemurgy Division, Chicago, Illinois. Typical analysis: moisture, 7.0 %; protein, 54 %; fat, 0.7 %; fiber, 2.6 %; carbohydrates, 29.7 %; d) DAS, dialdehyde starch.

stirring 12.5 parts of the isolated soy protein, oven-dried basis, in 67.4 parts of water and adding 1.2 parts aqueous ammonia, all parts by weight. The mixture was heated to 80°C for 20 min, cooled to 30°C and adjusted to 82.2 parts with water. It was then added to a pigment dispersion of 71% solids made up of 100 parts of clay in 40 parts water containing 0.2 part sodium hexametaphosphate. An initial low-shear agitation of the coating color was followed by high-shear agitation for 30 min for proper blending of the ingredients. Formulation was completed by adding 5 parts DAS premix by weight and mixing for 1 h. A similar coating color without DAS was also prepared at 50% solids for purpose of comparison.

The DAS premix was made by slurrying 10 parts of powdered DAS (Sumstar-190-lat), Miles Laboratories, Inc., Elkhart, Indiana), oven-dry basis, in 85 parts water by weight and heating to 90°C. After agitating and heating the slurry for 10 min at 90°C, it was cooled to 75°C and 1 part borax was added. Premix was stirred briefly before cooling to 25°C when the weight was adjusted to 100 parts with water.

The experimental coating color containing a mixture of soy flour and medium-viscosity isolated soy protein (Table 1) was also formulated at 50% solids. Selection of this coating color from among others composed of various combinations of soy flour and isolated soy protein was made on the basis that it furnished coatings having wax pick, brightness and wet-rub resistance more nearly like those of the reference coating. The experimental coating color was prepared by mixing 8 parts isolated soy protein, 8.3 parts soy flour, 72.2 parts water and adding 0.6 part aqueous ammonia, all parts by weight. The mixture was heated to 80°C for 20 min, cooled to 30°C and adjusted to 89.1 parts with water. The adhesive was added to 140.2 parts of the pigment dispersion, as previously described in the formulation for the reference coating color. Final mixing of the coating color was also done as previously described. All coating colors contained the equivalent of 12.5 parts protein per 100 parts clay. A duplicate experimental coating color that did not contain DAS was also prepared at 50% solids for purpose of comparison.

Coating Color Viscosity

Viscosity measurements of each coating color were made with a Brookfield LVF viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts) and with a Ferranti-Shirley Cone and Plate viscometer (Ferranti Electric, Inc., Electronics Division, Plainview, L.I., New York) 1 and 24 h after completion of each formulation.
Table 2. Rheological Properties of Coating Color and Surface Properties of Paper Coatings.

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>DAS (%)</th>
<th>Brookfield viscosity poises</th>
<th>Ferranti-Shirley viscometry</th>
<th>Critical wax strength number</th>
<th>Brightness (%)</th>
<th>Wet-rub resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6 rpm</td>
<td>60 rpm</td>
<td>Apparent viscosity (η_{1000/10} poises)</td>
<td>M' (dyne/sq cm/sec(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>Isolated soy protein</td>
<td>0</td>
<td>290</td>
<td>57</td>
<td>0.87</td>
<td>0.100</td>
<td>7.7</td>
</tr>
<tr>
<td>Isolated soy protein</td>
<td>4</td>
<td>500</td>
<td>93</td>
<td>0.98</td>
<td>0.092</td>
<td>8.0</td>
</tr>
<tr>
<td>Soy flour-isolated soy</td>
<td>0</td>
<td>190</td>
<td>46</td>
<td>1.12</td>
<td>0.133</td>
<td>6.3</td>
</tr>
<tr>
<td>soy protein</td>
<td>4</td>
<td>390</td>
<td>67</td>
<td>1.33</td>
<td>0.133</td>
<td>7.3</td>
</tr>
</tbody>
</table>

a) Equal to 12.5 parts protein per 100 parts clay; b) Percentage of DAS based on total protein; c) No. 4 spindle at 27°C; d) Viscosity 1 h after adding final ingredient; e) Coefficient of thixotropic breakdown; f) 1000 rpm; sweep time, 10 sec; medium cone, 27°C; g) Average of five tests; h) Reference coating color; i) Experimental coating color.

Ammonia added was adequate for dispersing both forms of protein present. When DAS was used in the coating color as the crosslinking or insolubilizing agent, putrefaction was retarded for at least 2 days. Without DAS, putrefaction as determined by odor was noted within 1 day.

Rheological data in Table 2 show that the viscosity of the experimental coating colors, with and without DAS, is lower at the lower rates of shear (6-60 rpm) but greater at higher rates of shear than that of the corresponding reference coating colors. Both the apparent viscosity at 1000 rpm for a sweep time of 10 sec (η_{1000/10}) and the coefficient of thixotropic breakdown (M') are slightly higher in the experimental mixture. The value M', calculated by the method of Thompson and Hansen [3], is proportional to the area of the hysteresis loop and, therefore, is a measure of thixotropy. In the absence of DAS, M' for the reference coating color is 0.100 (dyne/sq cm/sec\(^{-1}\)) compared with 0.133 for the experimental composition. Addition of DAS significantly increased the Brookfield viscosity of both coating mixtures. Rheograms of the reference and experimental coating colors made 1 h after completion of the formulations are shown in Figure 1. A comparison of the respective rheograms shows that the addition of DAS increased apparent viscosity, η_{1000/10}, of the reference coating color made from isolated soy protein from 0.87 to 0.98 poise and that of the experimental coating color containing soy flour-isolated soy protein from 1.12 to 1.33 poises. DAS in the coating mixture did not significantly affect either the general form of the rheograms (Figure 1) or M' (Table 2). These high-shear viscosity data, however, minimize the rheological differences in the coating compositions found by viscosity measurements made at low rates of shear (Table 2).

The viscosity of the experimental coating color without DAS remained relatively unchanged during 24 h (Figure 2).

![Figure 1. Ferranti-Shirley rheograms at 1 h for unmodified (a) and dialdehyde starch-modified (b) isolated soy protein and soy flour-isolated soy protein coating colors. Medium cone used at 27°C; 1000 rpm in 10 sec.](image1)

![Figure 2. Ferranti-Shirley rheograms for soy flour-isolated soy protein coating colors: unmodified (a) and dialdehyde starch-modified (b); - - - - 1 h and --- 24 h. Medium cone used at 27°C; 1000 rpm in 10 sec.](image2)
However, in the presence of DAS its apparent viscosity increased from 1.33 poises at 1 h to 1.60 poises at 24 h, and $M'$ increased from 0.133 to 0.158 dynes/sq cm/sec$^{-1}$. Where­
as the addition of DAS to the experimental coating color caused no significant change in thixotropy after 1 h aging (Figure 1), an increase was evident after 24 h aging (Figure 2).

All reference and experimental coating colors performed similarly during manual application to handsheet surfaces in the laboratory.

Coating Evaluation

The major surface properties of the coatings are compared in Table 2. Partial replacement of isolated soy protein by soy flour in coating color formulations, both with and without DAS, improved the brightness value but decreased the critical wax strength number and wet-rub resistance of the applied coating. DAS was responsible for appreciably increasing the wet-rub resistance of all coatings while moder­ately increasing the critical wax strength number and slightly reducing the brightness value of the coating. Bright­ness and critical wax strength number of the experimental coating containing DAS are almost identical to those for a similar coating containing 12 parts of a commercial-grade casein insolubilized with formaldehyde and applied to ident­i­cal-type stock [4].

Zusammenfassung

Dialdehydstärke in Papierbeschichtungsmitteln, die aus Sojamehl isolierten Sojaproteinklebstoff enthalten. Eine Kombination aus Sojamehl und isoliertem Sojaprotein wurde als Halbfertig in pig­mentierten Papierbeschichtungsmitteln untersucht, welche Dialdehydstärke (DAS) als Mittel zur Unlöslichmachung enthält. Eine Beschichtung aus 30 % Feststoff, bestehend aus 8,3 Teilen Soja­mehl, 8 Teilen isoliertem Sojaprotein und 0,5 Teilen DAS je 100 Teile Ton führte zu pseudoplastischem und thixotropem Fließ­verhalten der Beschichtungsfarben, die mehr tenne Proteinkleb­stoffe enthalten. Sowohl die Wachsaufnahmefestigkeit als auch die Naßabriebfestigkeit der Papierbeschichtung wurden verbessert und Fäulnisscheinungen wurden bei der Verwendung von DAS in der Rezeptur zurückgedrängt. Im Vergleich mit einer Beschichtung aus 12,5 Teilen isoliertem Sojaprotein und 0,5 Teilen DAS je 100 Teile Ton lagen die Werte für Helligkeit, Wachsfestigkeit und Naßabrieb­festigkeit außerordentlich günstig.

Résumé

L’amidon dialdéhyde dans le revêtement du papier, contenant un adhésif à base de farine de soja et de protéines isolées du soja.

Une combinaison de farine de soja et de protéines isolées du soja a été étudiée comme adhésif dans le revêtement pigmenté de papier, contenant de l’amidon dialdéhyde comme agent de l’insolu­bilisation. Une fumée de revêtement de 50 % de matière solide, constituée de 8,3 parties de farine de soja, 8 parties de protéines isolées du soja et 0,5 parties d’amidon dialdéhyde pour 100 par­ties d’argile conduit à un comportement de l’écoulement pseudo­plasique et thixotrope qui est caractéristique des couleurs de revêtement, qui contiennent des adhésifs préparés à base de protéines plus coémisses. La résistance à la fixation de cire ainsi que la résistance au gommage à l’état humide du revêtement de papier ont été améliorées et la puiréfraction a été retardée par l’utilisa­tion de l’amidon dialdéhyde dans la formule. La comparaison de la couleur, de la résistance à la fixation de cire et au gommage avec les produits contenant 12,5 parts de protéines isolées du soja et 0,5 parties d’amidon dialdéhyde pour 100 parties d’argile était particulièrement favorable.

References


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