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PAPER COATING COMPOSITIONS AND PROCESS

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This invention relates to an improved paper coating composition and to a process of coating a cellulosic web surface with such a composition. More particularly, our invention relates to the coating of paper with a composition comprising an acylated protein, and especially it relates to the coating of paper with a composition comprising phthalated isolated soya protein.

The art of coating paper has been developed to provide the printing industry with a suitable foundation material upon which inked impressions could be laid down. Usually, coated paper is prepared by mixing finely-divided solid mineral substances with an adhesive and applying this mixture to the surface of the paper. In this manner, the individual fibers on the web surface of the paper are coated by the mineral substances and the hollows between the fibers are filled in, so that after calendaring, a smooth continuous surface is provided which is receptive to printed ink and which permits an accurate reproduction of the printing plate to be obtained. The adhesive serves to bind the particles of mineral substance to the web surface to prevent them from being "picked" during the printing operation.

In the preparation of the coating compositions of the past the adhesive, which may be casein, isolated soya protein, soyabean meal, or the like, is first suspended in water, then dispersed ("cut") by adding various known cutting agents and the finely-divided mineral substances, clay, titanium dioxide, blanc fixe, satin white and the like, as well as tinting materials, preservatives, anti-foaming agents, etc., are added to the aqueous "cut" of the adhesive. This coating composition or "coating color" as it is sometimes referred to, is then applied to one or both sides of the paper, the coating being evenly distributed by means of doctor blade knife, air-knife, squeeze rolls and/or brushes, and the coated paper dried by means of heated rolls or heated air in an oven or in festoons in a drying gallery. The dried paper is usually calendared to provide the smooth finished surface receptive to the printing operation.

Prior to the present invention, casein, starch, animal glue, and isolated soya protein were the main adhesives used in the coating of paper. Of these, glue has fallen into disuse, principally because of the difficulties attendant upon its use. Starch is used in quantity for the coating of paper wherein quality, and especially water resistance is not of prime concern. Casein and isolated soya protein have become the adhesives of choice for quality coated paper in this art, due in part to the ease with which coatings prepared therewith can be made water resistant.

Commercially available casein is subject to wide variation in quality and hence is troublesome to utilize in routine plant practice. Furthermore, coating compositions containing casein lose their fluidity, that is, they tend to be dilatant under pressure and shear when the freshly coated paper is passed between the smoothing rolls. This undesirable attribute is accentuated as the solids content of the coating increases. Since it is desirable to use a coating composition of as high a solids content as feasible, for reasons of quick drying and greater speed of the coating machines, this dilatant character of casein-containing coating compositions is a serious drawback to its use in this field.

Isolated soya protein (such as "Alpha" protein, a product of The Glidden Company) on the other hand, gives rise to thixotropic coating compositions and by virtue of the fact that it is a product of a carefully controlled chemical processing operation, it is not subject to the wide fluctuation in viscosity of its alkaline dispersions as is casein. However, save for special grades of this product, the viscosity characteristics of "Alpha" protein are such as to effectively limit the solids content of coating compositions to a point comparable to that obtained with casein. Further, when using isolated soya protein, considerable care must be exercised or specialized mixing equipment must be used when preparing the coating composition to prevent "buckling" or excessive thickening of the mixture, especially when working in the upper range of solids content.

We have now found that when dilute alkaline solutions of isolated soya protein are treated under acylating conditions with dicarboxylic acid anhydride, an acylated protein material appropriate for coating usage is obtained. This acylated protein, when "cut" with alkalies, disperses more readily than the untreated isolated protein and the "cut" has a viscosity surprisingly less than the untreated isolated protein. Furthermore, when used as the adhesive component of a paper coating composition, the solids content of the composition can be increased to a surprisingly high degree while preserving the desirable fluidity of the composition. Since this high solids content compostion retains the thixotropic character of the original isolated soya protein composition, the desired and long-sought advantages of a high solids coating composition have been obtained. Additionally, we have found that acylated-protein-containing coating compositions have increased adhesiveness as compared to those containing unacylated isolated soya protein, and in fact, in this respect the improved coating compositions are equal or superior to coating compositions containing high-grade casein as the adhesive.

Accordingly, the present acylated-protein-containing coating compositions of our invention are characterized by increased fluidity and adhesiveness whereby the extent to which isolated soya protein can be used as a raw material in the paper coating art has been surprisingly increased.

The herein-described improvements in isolated soya protein have resulted in the development of paper coating compositions especially suitable for coating paper by the machine-coating process. As indicated in Technical Bulletin 1043, U.S. Dept. of Agriculture, "Marketing Potential for Oilseed Protein Materials in Industrial Uses," machine-coating of paper was, prior to 1951, largely confined to the use of starch as the adhesive. Isolated soya

protein and casein, because of the difficulty of preparing high solids compositions (a prime requisite in machine-coating) had been difficult to utilize in this important use. Our new compositions, because of their improved viscosity characteristics which permit the formulation of high solids coating compositions, are readily adaptable to machine coating paper mill equipment. Moreover, with this development of the machine-coating of paper, and of coated paper which is readily rendered water-resistant, an additional improvement in this field has been successfully demonstrated.

The following examples illustrate the procedures of our invention:

EXAMPLE 1

Preparation of acylated protein

Soybeans were extracted in a known way, which constitutes no part of our invention, with an organic solvent to remove substantially all of the oil therein. One hundred parts (by weight) of the extracted residue, in the form of flakes, were agitated for 1.5 hours with a suspension of 2.5 parts of lime and 1400 parts of water at 80° F. The resulting slurry was filtered over screens to recover 1200 parts of lime liquor. The spent flakes were reslurried in a mixture of 1150 parts of water and 2 parts of sodium hydroxide at 120° F. for ten minutes. This slurry was separated by screening into 950 parts of caustic liquor and a residue of spent flakes. The latter were washed by reslurrying in 1200 parts of water at 145° F., and the slurry was filtered over screens to yield a wash liquor and washed spent flakes. These were pressed to give an additional 100 parts of wash liquor. All of the wash liquor (1300 parts) was added to the lime liquor, and the combined mass was rendered acid to a pH of 4.6 by the addition of sulfur dioxide. The precipitate which formed was allowed to settle, and the supernatant whey (1950 parts) was decanted from the curd (550 parts). The wet curd was reslurried in the 950 parts of caustic liquor, identified above, and to this slurry was added 3.4 parts of lime and 4.8 parts of soda ash. The mixture, containing about 33 parts of protein, was heated and agitated at 120° F. for 6 hours, during which period it was clarified by centrifuging. A solution of 4.125 parts of phthalic acid anhydride dissolved in 200 parts (by volume) of acetone was added dropwise to the hot protein solution during a period of about 25 minutes. During this addition, the pH of the mixture was maintained at 9.5, as closely as feasible by the dropwise addition of 10% aqueous caustic soda. The reaction mixture was agitated for about 35 minutes thereafter to complete a seven-hour hydrolysis period.

The mass was then rendered acid to a pH of 4.2 to 4.4 by the addition of sulfur dioxide. The resultant slurry was permitted to settle for about 16 hours and then after the whey had been decanted the curd was pressed to a cake, granulated and then dried at 140° F.

In similar manners, acylated isolated soya proteins were prepared using in place of phthalic acid anhydride

an equal weight of maleic acid anhydride or of succinic acid anhydride.

In another treatment, the dibasic acid anhydride was added to the alkaline protein solution as a finely ground powder, instead of as a solution in acetone, over a period of about 20 minutes. In this manner, acylated protein of comparable properties was obtained.

In such instance, the acylated protein material when used as a component of a paper coating composition gave coatings which were superior with respect to adhesion compared to similar coatings prepared using "Alpha" protein, and approximately equal to the adhesion of coatings prepared using "Sheffield" casein.

EXAMPLE 2

Preparation of coating composition and coated paper

The acylated proteins prepared as described in Example 1 above were tested in paper coating compositions as follows:

The protein was thoroughly wetted out in water by mixing 50 grams of the protein in 200 grams of water for five minutes, at about 75° F. Thereafter, a solution containing 1 gram 28% aqua ammonia was added and followed with 6 grams of sodium carbonate. Then 50 grams of water was added to the protein dispersion and the mixture was heated to and maintained at 135° to 140° F. for 45 minutes. To 150 grams of the "clear," a slurry of 200 grams of "HT" Clay (commercial coating clay of medium size, product of Minerals and Chemicals Corp. of America, Edgar Div.) in 212 grams of water was added, and the mixture was agitated until uniformly blended.

The viscosity at 90° F. of a 40% solids coating mixture was determined with a Brookfield viscosimeter at 30 r.p.m. and 60 r.p.m.

The coating composition was applied to three commercial grades of paper using a Meyer Rod No. 22. The coated base stock was dried, calendared and conditioned at 73° F., 50% RH for about 3 hours (see TAPPI Standard T402m), before subjecting them to the wax test for surface strength of paper (see TAPPI Standard T459m–45).

The results of these tests for the acylated proteins, an "Alpha" protein standard, Sheffield casein, and an Argentine casein, are set out in Table I below:

TABLE I

Test	"Alpha" Protein	Phthalated "Alpha" Protein	Maleated Protein	Succinated Protein	Casein	
					Sheffield	Argentine
Viscosity at 90° F.:						
30 r.p.m.	450	170	78	150	110	245
60 r.p.m.	314	135	72	124	155	[1] 164
Wax Pick Paper: [2]						
A	4 vsl−	5+	6 sl−	6 vsl−	5	6−
B	5 sl−	6 sl−	6−	6	6−	6−
W	5	7	7+	8 vsl−	6+	7−

[1] Apparently an anomalous result.
[2] Base stock used in these tests were commercial grades of uncoated paper from three manufacturers.

Analogous results of viscosity and "pick tests" on various paper stock were obtained by using as cutting agents for the proteins 2% aqua ammonia plus 15% soda ash or 5.5% sodium hydroxide in place of the above mixture of 2% aqua ammonia plus 12% soda ash.

EXAMPLE 3

Acylated proteins using other dibasic anhydrides as the acylating agent were prepared as described in Example 1 above. The resultant products were used as the adhesive components in paper coating compositions prepared and tested as described in Example 2 above.

The results of the tests are set out in Table II below:

TABLE II

Test	"Alpha" Protein acylated with—						
	Control [1]	TCP [2,3]	F.G. PAA [4]	FL. PAA [5]	THP [6]	NA [7]	Sheffield Casein
Viscosity at 90° F.:							
30 r.p.m.	300	165	200	220	340	270	160
60 r.p.m.	192	142	149	148	230	132	124
Wax Pick Paper:							
A	4	6 sl−	6 sl−	6 sl−	6 vsl−	4+	6−
B	5	6	6 sl−	6 vsl−	6 vsl−	5 sl−	6
W	5+	7 sl−	7 sl−	7−	7 sl−	6	7 vsl−

Legend:
[1] All proteins "cut" with 2% NH_4OH + 15% Na_2CO_3 by weight on protein.
[2] Ten percent by weight of acylating agent on the protein was used in all preparation except for "TCP" protein, in which instance 15% of the acylating agent was used.
[3] "TCP" represents tetrachlorophthalic acid anhydride.
[4] "F.G. PAA" represents phthalic acid anhydride ground to 40 mesh.
[5] "FL. PAA" represents phthalic acid anhydride flakes (commercial grade).
[6] "THP" represents tetrahydrophthalic acid anhydride.
[7] "NA" represents Endo-cis-bicyclo (2,2,1)-5-heptene, 2,3-dicarboxylic anhydride—Nadic Anhydride" a product of National Aniline Div., A.C. and D.

Hexahydrophthalic acid anhydride, 3-nitro-phthalic acid anhydride and dodecenyl succinic acid anhydride, when used in a similar manner to acylate isolated soya protein, gave coating compositions of improved adhesive characteristics, also.

EXAMPLE 4

The improvement of an isolated protein by acylation is not limited to isolated soya protein. Casein, too, can be treated with dibasic acid anhydrides to yield improved adhesive characteristics in paper coating compositions.

To a hot (130° F.) slurry of Sheffield casein (750 grams) in water (7 gallons) 10% aqueous caustic soda (580 ml.) was added during 25 minutes. The mixture was agitated for 20 minutes thereafter, and the dispersion was divided into 3 equal portions. One portion was reserved as a control, another was treated under acylating conditions with finely ground phthalic acid anhydride (25 grams) and the third portion was acylated with crystalline maleic acid anhydride (25 grams). The acylations were carried out over a period of just over one hour after which the proteins were precipitated by addition of sulfur dioxide to a pH of 4.4 in the control run, to 3.3 in the phthalic run and to 3.7 for the maleic run.

The precipitated acylated caseins were worked up as described in Example 1 and were then "cut" with 2% ammonium hydroxide and 15% soda ash as described in Example 2 above. Clay in an amount 8 times that of the casein was then added. These mixtures were tested as described in Example 2 also. The results of such tests are set out in Table III below:

TABLE III

Test	Casein Control	Phthalated Casein	Maleated Casein	Sheffield Casein
Viscosity 90° F.:				
30 r.p.m.	105	96	612	88
60 r.p.m.	220	380	1680	231
Pick Test:				
Paper A	4+	6+	7 vsl−	5+
Paper B	5+	6+	6+	6 sl−
Paper W	6 sl−	7	7	6

These results indicate that the acylated caseins as in the case of acylated soya protein give rise to paper coatings having improved adhesion. In these instances, the acylated casein coatings are superior to both the unacylated control Sheffield casein as well as to the Sheffield casein itself. It will be noted that the viscosity of the acylated "coating colors" is greater than that of the untreated Sheffield casein "color," a different from that noted between acylated and unacylated soya protein. This difference is indicative of the dilatant character of both acylated and unacylated casein.

This acylation procedure can be made a step in the isolation of a modified casein from skim milk. For example, the skim milk can be made alkaline, acylated with a suitable acylating anhydride as described in the examples above, and the modified casein isolated according to known procedures disclosed in the art of preparing casein from skim milk.

EXAMPLE 5

In this example peanut protein has been treated with phthalic anhydride. For this purpose, peanut protein was prepared from peanut meal (from Southern Utilization Branch USDA—Sample No. 5429–E–3–2(14), Sodium hydroxide treated defatted meal). Three 500 g. portions of the meal were extracted with 13 l. of water each at 130° F. for 1.5 hours. The mixture was then centrifuged, clarified liquor combined (32.2 l.) and the protein precipitated with SO_2 at pH 4.6. After standing overnight, 30 l. of whey were decanted. Then 2.6 l. of water was added to the settled curd (2.4 l. volume). The solids ran 12.325% or 616.25 g. Twenty l. of water at 120° F. was added to bring the curd slurry to a total volume of 25 l. (pH 5.1). With mechanical agitation, 300 ml. of sodium hydroxide solution (10 g./100 ml.) was added to disperse the protein. After ten minutes of stirring the pH was 11.1. This alkaline liquor was divided into two portions; 10 l. (R4–7A) for treatment with phthalic anhydride and 15 l. (R4–7B) to serve as a control. The treatment consisted of adding 25 g. of the fine-grind anhydride.

Batch	Anhydride	Initial pH	Reaction Time, hr.	Final pH	Pptn. pH
R4–7A	Phthalic [1]	11.1	1	[2] 7.9	4.3
R4–7B	Control	11.1		11.1	4.4

[1] Added over a five minute period.
[2] Ten minutes after the end of the addition, the pH had dropped to 5.8, therefore added 60 ml. of sodium hydroxide solution (10 g./100 ml.) to bring pH to 8.9.

The proteins were precipitated with SO_2, allowed to settle overnight, the whey separated, the curd pressed, granulated and dried at 140° F. After moisture equilibration, the proteins were ground to pass 40 mesh. The proteins were then analyzed.

Protein	Wgt. Yield, g.	Percent Moist.	Percent Prot.	Viscosity	pH	DR
R4–7A	276.5	8.58	97.86	64.4"	9.1	Trace.
R4–7B	[1] 281.3	8.00	101.03	40.8"	9.4	Trace.

[1] The yield of control protein when converted to a basis equivalent to the treated protein amounts to 254.2 g.

The weight pick-up on the treated peanut protein appears normal; however, the finished protein shows no great change in anionic character. In this instance, the anhydride treatment resulted in a viscosity increase in dispersions of the protein. Inspection of the protein analysis reveals that the nitrogen to protein conversion factor is considerably different than the 6.25 customarily used for soy proteins and casein. Viscosity and adhesion data of paper coatings are shown in the following table:

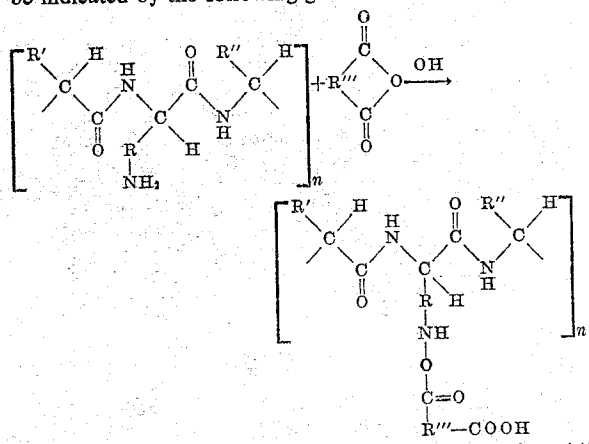
Acylated peanut protein—paper coatings

[12.5 parts acylated protein; 100 parts coating clay; cutting agent: 2% NH_4OH plus 15% Na_2CO_3 balance water.]

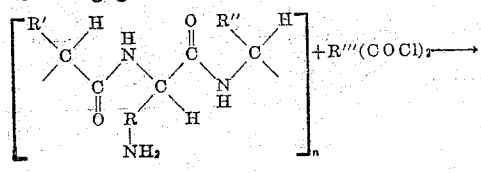
	R4-7A	R4-7B
pH of color	9.3	9.5
Viscosity at 90° F., 30 r.p.m.	600	212
Viscosity at 90° F., 60 r.p.m.	420	184
Wax Pick Test, Paper A	6+	4+
Wax Pick Test, Paper B	6 vsl−	4+
Wax Pick Test, Paper W	6+	6 sl−

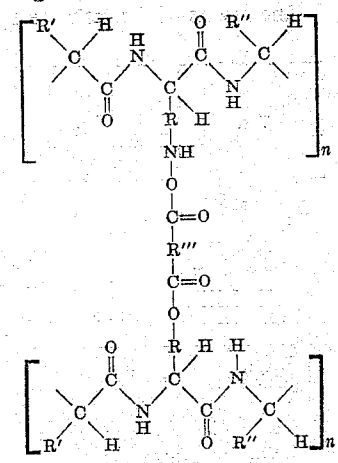
It will be readily seen from the foregoing examples that improved coating compositions have been provided for the preparation of coated paper and like materials. The invention, however, is not limited to the specific variations cited in these examples. Our invention, broadly speaking, contemplates coating compositions containing at least one acylated protein substance as the adhesive component.

Acylation of protein is, of course, old in the art. We have now found, however, that by selection of the acylating agent and of conditions of acylation such that cross-linking of the protein molecule is substantially excluded, acylated protein products which are useful in our novel coating compositions are provided. Anhydrides of α,β-dicarboxylic acids are especially desirable in this connection, for under acylating conditions only one of the carbonyl groups reacts with an amino or other reactive moiety of the protein molecule leaving the second carbonyl group as a free carboxylic acid group (or in the presence of alkali as the alkaline salt). In effect, the anionic character of the protein molecule is altered by acylation with the dibasic acid anhydride. The free amino or other groups of the protein are to some effective extent replaced by carboxylic acid groups. This can be indicated by the following general formula:



Other types of acylating agents, such as dibasic acid halides, lead most likely to cross-linking and hence such acylating agents are not suitable for use in our procedure. This undesirable cross linking can be indicated by the following general formula:





Inasmuch as it is well known that cross-linking causes an increase in the viscosity of a macromolecule, it follows that in the present invention such an effect is to be avoided as completely as possible. Accordingly, we have found that by reacting relatively dilute solutions/dispersions of isolated proteins (that is to say up to about 10% concentrations) and by using α,β-dicarboxylic acid anhydrides as acylating agents, the acylated soya protein product is obtained with substantially no cross-linking. Alkaline dispersions, i.e., "cuts" of such proteins are characterized by viscosity characteristics lower than the untreated protein source material and, further, when such treated proteins irrespective of their origin are incorporated into coating compositions, such compositions have surprisingly high fluidity and give rise to coated products which have excellent adhesion properties.

The process of our invention which has enabled us to provide the improved isolated, acylated hydrolyzed soya protein described herein in connection with its use in coatings on paper and analogous cellulosic products is described and claimed in our copending application Serial No. 570,970, filed March 12, 1956.

The coating compositions of our invention can be formulated with finely-divided mineral substances or clays other than those used in the illustrative examples. Further, pigments such as titanium dioxide, lithopone, blanc fixe, can be used either alone or in admixture with such clays.

Antifoam agents to reduce or prevent foaming, waxes to improve printability, coloring matters, wetting agents, and the like adjuvants commonly used in coating compositions for cellulosic web surfaces can be incorporated in the compositions of our invention. Such are within the purview of the skilled workers in this field.

The present invention has been described by means of certain examples which are intended to be illustrative rather than limiting in nature. Further, certain aspects of our invention have been explained by recourse to theoretical considerations. However, it is to be distinctly understood that we do not intend to be bound by the ultimate correctness of such theoretical explanations. In short, our invention is not to be limited except as indicated in the appended claims.

Having described our invention what we claim is:

1. The process of coating a web surface comprising applying to a surface thereof an aqueous anionic dispersion of at least one acylated protein and a finely divided inert filler, the acyl moiety of said protein being derived solely from a dibasic acid anhydride employed to acylate said protein.

2. The process of claim 1 in which the said anhydride is an alpha, beta-dicarboxylic acid anhydride.

3. The process of claim 2 in which the anhydride is phthalic acid anhydride.

4. The process of coating a web surface comprising applying to a surface thereof an aqueous anionic dispersion of at least one acylated protein and a finely divided

inert filler, said protein being isolated hydrolyzed soya protein, the acyl moiety of said protein being derived solely from the dibasic acid anhydride employed to acylate said protein, the acylation of said protein being achieved by reacting said anhydride with a dilute aqueous dispersion of said isolated protein while continuously maintaining the reaction menstrum alkaline.

5. The method of claim 4 in which the dibasic acid anhydride is an alpha, beta-dicarboxylic acid anhydride.

6. The method of claim 4 in which the said anhydride is phthalic acid anhydride.

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