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An Improvement of Low Molecular Weight Yeast Protein on Paper Coating Application

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Modified yeast protein could be used for paper coating, but some properties such as IGT pick resistance, wet pick and wet rub resistance were not so good as that of milk casein. In order to improve these characteristics, sodium *arginate*, sodium carboxy methyl cellulose or milk casein was used, The addition of milk casein (modified yeast protein 10 %: milk casein 5%) showed the best result with a flow curve, less non-Newtonian such as weak thixotropic flow, near to that of milk casein and the IGT pick resistance, wet pick or wet rub resistance were greatly improved compared with modified yeast protein itself. Wet pick resistance varied from 1.5 to 3.6, very near to that of milk casein (3.5), and wet rub resistance was from 7-10 to 10-13 compared with that of milk casein which was 12. The IGT pick resistance was from 111-121 to 155, while milk casein was 238. In the case of milk casein addition, the 2 hrs modification (10 % yeast protein, 1 % NaOH, 60°C) was clearly most suitable method for mixing with milk casein, the loss of protein which could not be recovered by acid-precipitation was 23%. The modified yeast protein obtained with this method was good in color, purity and very transparent when dissolved in alkali solution. And from the flow curve of modified yeast protein and milk casein mixture solution, it was obvious that this sample was more appropriate applied with a roal coater than a brush or air knife coater.

INTRODUCTION

As reported in the previous paper (Khai *et al.*, 1974), modified yeast protein could be used not only for food but also in industry as paper coating adhesive. In the case of paper coating application, the IGT pick resistance, wet pick resistance and wet rub resistance were not so good as those of milk casein. The aim was to improve these characteristics ; moreover, the modified yeast protein in the previous method (Khai *et al.*, 1974) was not good in color and not simple, due to the use of ion exchange resin, this paper, thus presents an other simpler method, for producing modified yeast protein, good in color, purity and very transparent, when dissolved in alkali solution. From the results in sheet properties and printability using the modified yeast protein of this method with the addition of a small amount of milk casein, it was obvious that this method is good for producing modified yeast protein, which applies to paper coating.

MATERIALS AND METHODS

Materials

a) Baker's yeast protein was extracted from ***Saccharomyces cerevisiae,*** produced by Kanegafuchi Chemical Industrial Co., Ltd.

b) Sodium arginate (SA), sodium carboxy methyl cellulose (CMC) was produced by Ishizu Chemical Co., Ltd., and methyl cellulose (MC) was of Ishida Chemical Co., Ltd.

c) Commercial milk casein was product of Kishida Chemical Co., Ltd.

Sample preparation

Yeast protein and modified yeast protein were prepared by the method shown in Fig. 1. The modified conditions were followed using the results of the previous paper (10% yeast protein, 1% NaOH, 60°C), in order to pursue the variation of the flow curve and viscosity of modified yeast protein, yeast protein was hydrolyzed at various heating intervals. After hydrolyzing with alkali (NaOH), H_2O_2 was added to decolor the solutions (Nomura et ***al., 1972***; Hayakawa et ***al., 1973)*** and the proteins were recovered by acid-precipitation (pH 4.5) by HCl. The proteins, after washing with de-ionized water twice, were dehydrated rapidly by acetone and were called as follows:

MYP- 2 : 2 hrs modified yeast protein
MYP- 7 : 7 hrs modified yeast protein
MYP- 8 : 8 hrs modified yeast protein
MYP-10 : 10 hrs modified yeast protein

Flow curve of modified yeast protein

Weissenberg-Rheogoniometer (Iwamoto Seisakusho, Co., Ltd.) was used for these determinations. The shear rate and shear stress were calculated by the following equations (Kobunshi Gakkai Iinkai, 1965)

$$S = T/2\pi h r_b^2$$

$$D = \gamma_a(1+\Delta S)$$

with

$$\gamma_a = 7.0420$$

$$\Delta S = k_1 d\log\phi_\alpha/d\log S + k_2(d\log\phi_\alpha/d\log S)^2$$

$$k_1 = \left[(\alpha^2-1)/2\alpha^2\right]\left[1+(2/3)\ln\alpha\right]$$

$$k_2 = \left[(\alpha^2-1)/6\alpha^2\right]\ln a$$

where,

s : shear stress
D : shear rate
T : torque
h : the length of the internal tube put into the sample
r_b : internal tube radius
r_a : external tube radius
k_1, k_2 : apparatus coefficient
α : ratio of external tube radius to internal tube radius
ϕ_α : apparent fluidity

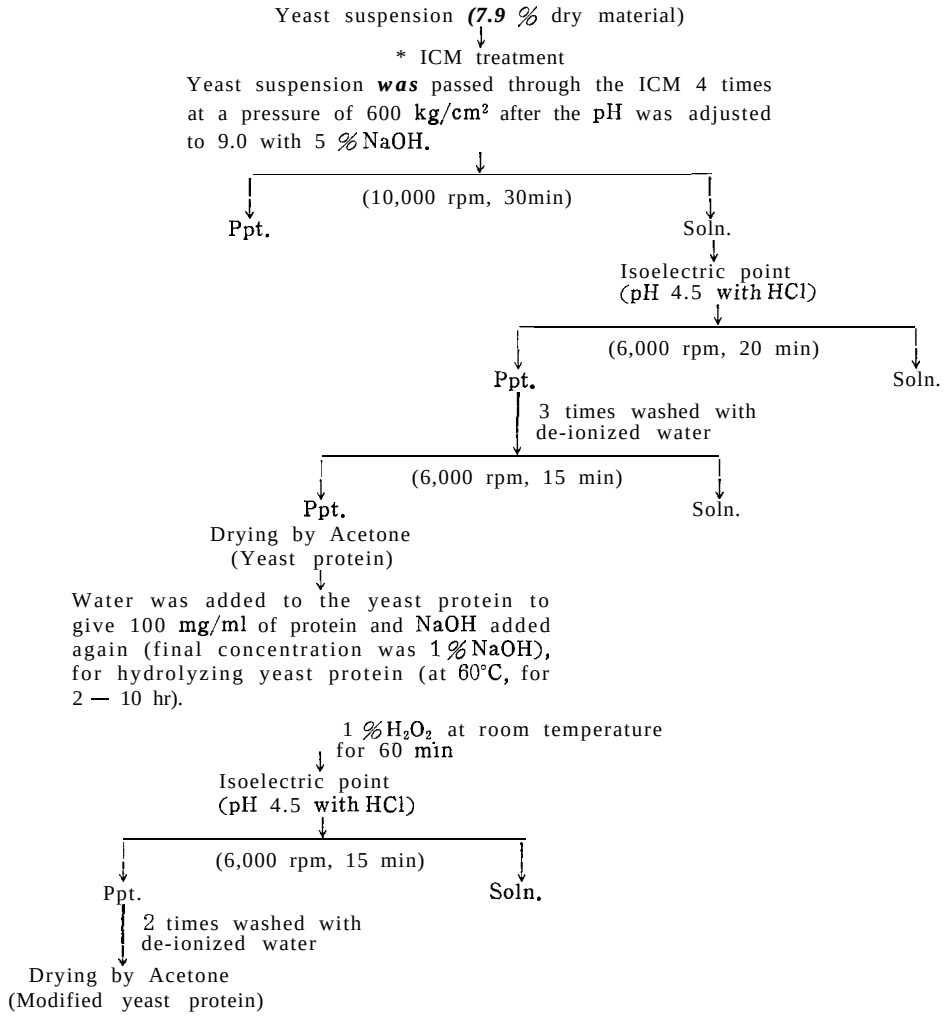

Fig. 1. Preparation of modified yeast protein. *ICM: Impact-Cell-Mill

Gel filtration of modified yeast protein

Sephadex G-200 was used to obtain the gel filtration chromatogram of these modified yeast proteins. A column of the Sephadex (1.5×90 cm) was equilibrated with 0.076 M Tris-citrate buffer (pH 8.6) containing 0.4M NaCl. A flow rate 3 ml/hr was maintained using a restricting screw cock. Every 5 ml aliquot was collected with a fraction collector and absorbance at 280 nm was measured with a Hitachi Perkin Elmer 139 UV Vis Spectrophotometer.

Properties of the binder of the modified yeast protein for coated paper

The conditions for determining these properties were the same as those of A, B, C and D modified yeast protein, described in the previous paper (Khai *et al.*, 1974).

RESULTS

General analysis of modified yeast proteins

As shown in Table 1, the moisture content of the acetone dried yeast proteins was 6-7%, while the moisture content of lyophilized yeast protein was twofold larger. Thus, acetone drying has a better effect in storage. Modified yeast protein was also higher than yeast protein in purity and lower in fat or ash content. The recovery of modified yeast protein by the acid-precipitation is shown in Table 2. A solution containing 10% yeast protein was hydrolyzed by 1% NaOH at 60°C for 1 hr and showed a rapid hydrolysis, but from 2 hrs, the hydrolysis became less rapid. Ten hrs modification gave a hydrolysis of only 28.5%, compared to 20% of 1 hr modification.

Table 1. Compositions of modified yeast protein,

Sample	Moisture (%)	Protein (N×6.25)[b] (%)	Fat [c] (%)	Ash (%)
Unbleaching yeast protein[a]	14.70	86.91	1.11	2.96
Bleaching yeast protein	6.00	89.74	0.34	3.04
Modified yeast protein (2 hr)	6.16	91.74	0.27	1.04
Modified yeast protein (4.5 hr)	7.64	93.28	0.30	1.33
Modified yeast protein (7 hr)	6.74	92.37	0.39	1.35
Milk casein	11.03	94.40	0.34	0.17

a) Lyophilization
b) Micro Kjeldahl method
c) Ether extraction

Table 2. Recovery of modified yeast protein. Yeast protein was hydrolyzed with NaOH (final concentration of yeast protein was 10 % and of NaOH was 1%), at 60°C for various heating time.

Heating time (hr)	Recovery of modified yeast protein (%)
0	100.00
1	
2	80.22 77.06
3	76.27
4	75.48
6	74.69
8	**73.10**
10	**71.52**
20	**66.77**

Flow curves of modified yeast proteins

The paper coating adhesive such as protein was generally used in high concentration (about 15%) at pH 9 – 10, adjusted with NH_4OH. The flow curves of modified yeast proteins obtained from the conditions (10% yeast protein, 1% NaOH, 60°C, 2 – 10 hrs) are shown in Fig. 2. In this figure, 15% milk casein

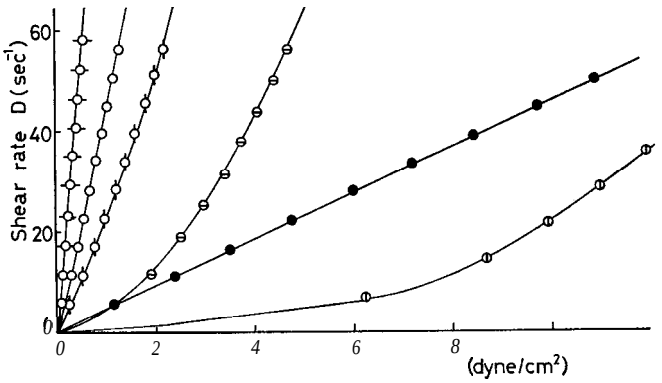

Fig. 2. Flow curve of modified yeast protein, measured at 30°C. ① 4 hrs modification; ⊖ 4.5 hrs modification; ○ 6 hrs modification; ○ 8 hrs modification; ⊙ 10 hrs modification; ● milk casein.

showed a Newtonian flow, but the modified yeast protein formed a gel till near 4 hrs modification. From 5-8 hrs modification, in spite of a lower viscosity than that of milk casein, there still existed a flow curve of non-Newtonian as thixotropic flow, and from above **10** hrs hydrolysis, the flow curve tended to Newtonian.

Effect of CMC, MC, sodium arginate or milk casein on flow curve of modified yeast protein

Generally, the printability of a coated paper was improved by CMC as reported in some papers (Tanaka et ***al.***, 1967 ; Higham, 1968), so that in order to improve the qualities of these characteristics, CMC, MC, sodium arginate or milk casein should be used. As shown in Fig. 3, there is an enhancing effect

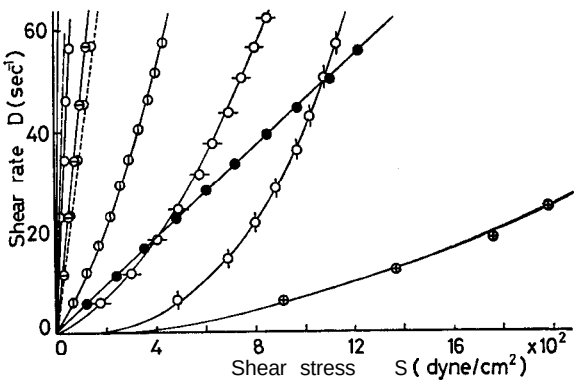

Fig. 3. Effect of CMC, MC, Sodium arginate and Milk casein on flow curves of various modified yeast proteins, measured at 30°C. ○ MYP-10 (15%); ⊖ MYP-8 (15%); ● Milk casein (15%); — CMC (0.5%); - - - SA (0.5%); ⊕ MYP-8 : SA (14.5% : 0.5%); ⊙ MYP-8 : CMC (14.5% : 0.5%); --○-- MYP-8: MC (14.5% : 0.5%); ⊙ MYP-10 : SA (14.5%: 0.5%); ① MYP-10 : CMC (14.5% : (0.5%)

between the modified yeast protein and CMC, MC or sodium arginate. The flow curve of 10 hrs modified yeast protein was Newtonian flow, but when 0.5 % CMC, MC or sodium arginate were added, the flow curve tended to non-Newtonian and sodium arginate has an effect stronger than the others. In the case of the addition of milk casein, 2 hrs modified yeast protein (10 : 5 or 9 : 6) has a flow curve, near to that of milk casein as shown in Fig. 4. Next, the influence of temperature on the flow curve of modified yeast protein or mixture of modified yeast protein and CMC or milk casein is shown in Fig. 5. A mixture of modified yeast protein and CMC (14.5 : 0.5), showed a non-Newtonian flow till 50°C, but milk casein addition (10 : 5) showed a Newtonian flow, from a temperature above 40°C, and a less non-Newtonian flow at 30°C, while milk

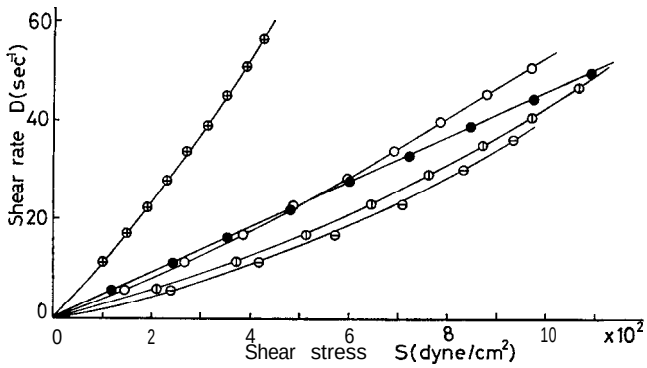

Fig. 4. Flow curves of various mixtures of 2 hrs modified yeast proteins and milk casein, measured at 30°C. ● Milk casein (15%) ; ○ MYP-2: Milk casein (9%: 6%); ⊕ MYP-2 : Milk casein (10% : 5%) ; ⊖ MYP-2 : Milk casein (11% : 4%) ; ⊕ MYP-3 : Milk casein (10% : 5%)

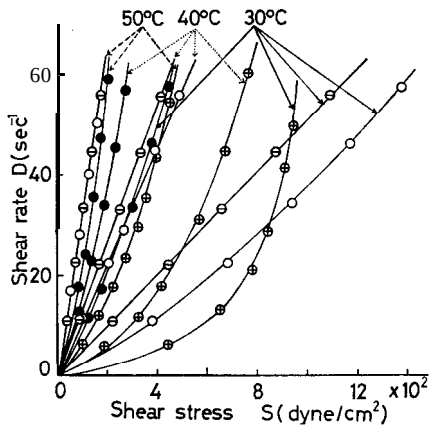

Fig. 5. Effect of temperature on the the flow curves of the mixture of modified yeast proteins and milk casein or CMC. ⊖ Milk casein ; ○ MYP-2: Milk casein (10% : 5%) ; ⊕ MYP-8 : CMC (14.5% : 0.5%) ; ● MYP-10 : CMC (14.5% : 0.5%)

casein (15%) always showed a Newtonian flow over this range of the temperature. Again, in order to know the variational degrees of modified yeast proteins, aging time effects on its flow curves were also investigated and the results are shown in Fig. 6. When the milk casein left at room temperature for 2 hrs and 19.5 hrs, the flow curve tended from Newtonian flow to a slightly non-Newtonian flow, while the mixture of modified yeast protein and milk casein (9 : 6 or 11 : 4) showed a larger variation in the flow curve, when left at room temperature for 2 – 9 hrs, but not so much as modified yeast protein only.

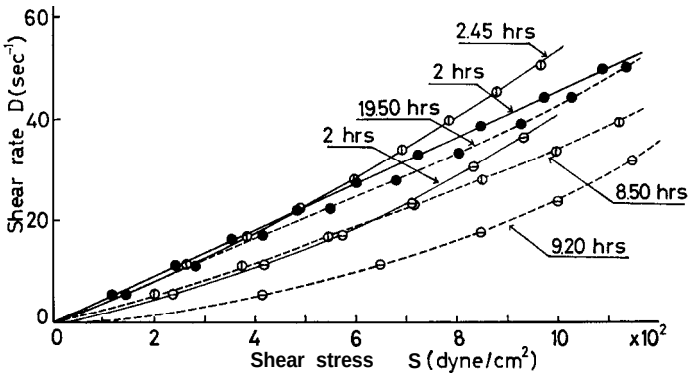

Fig. 6. Effect of aging time on the flow curves of the mixture of modified yeast protein and milk casein, measured at pH 9.8 (29°C). ● Milk casein; ⓘ MYP-2 : Milk casein (9% : 6%); ⊖ MYP-2 : Milk casein (11% : 4%)

Gel filtration of modified yeast protein and coating casein

In order to know the extent of the modification of yeast protein, the chromatogram of gel filtration (Sephadex- **200)** should be used to compare some modified yeast proteins with milk casein or coating soybean protein (Kato, 1969 ; Moriya, 1969). The result is shown in Figs. 7 and 8. In this case, a 0.5% concentration of yeast protein or milk casein was used, but when dissolved in alkali solution (ammonia) to mix with coating colors, coating protein was positively associated, rather than dissociation as in the case of dilute solution. From the results in Figs. 7 and 8, modified yeast protein and yeast protein showed a peak at effluent volume of 60–80 ml. The dimension of the peak decreased following more modification, and the dimension of the chromatogram behind the peak was comparatively larger, similar to that of coating soybean protein. Again, the distribution of molecular weight of yeast protein, following the modifications are shown in Table 3. The larger portion (MW 〉200,000) was decreased from 64.8%–30% as compared with that of smaller portion (MW 〈25,000), which was increased from 10.5 to 25%–35% in 2-7 hrs modification. In this case, the milk casein has a portion of MW) 200,000 was 40.3% and of MW 200,000–100,000 was 40% and of MW 100,000–25,000 has 15.6%. The last two portions were the dimension **of** the second peak of milk casein.

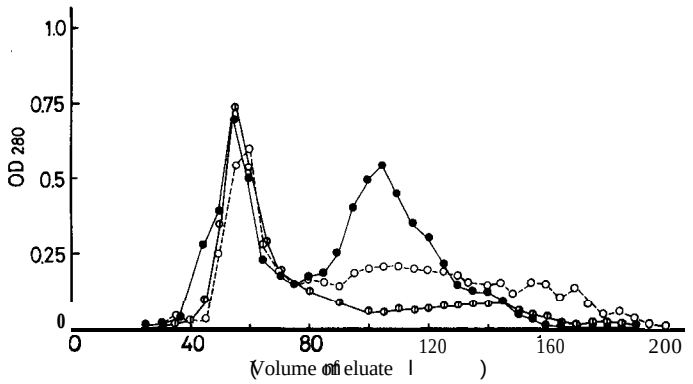

Fig. 7. Column Chromatograms of yeast protein, milk casein and coating soybean (low viscosity) protein with Sephadex G-200 (1.5×90cm). 0.076M Tris-citrate buffer (pH 8.6) containing 0.4M sodium chloride. Flow rate : 3 ml/hr. Fraction volume : 5 ml. ⓘ Yeast protein ; ● Milk casein ; ○ Coating soybean protein

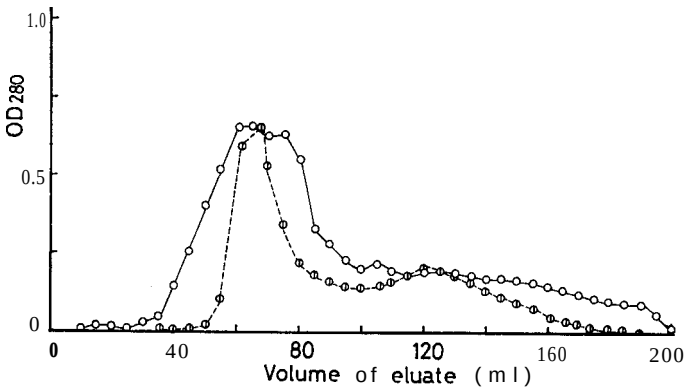

Fig. 8. Column Chromatograms of modified yeast protein with Sephadex G-200 (1.5x 90cm). Eluant : 0.076M Tris-citrate buffer (pH 8.6) containing 0.4M sodium chloride. Flow rate : 3 ml/hr. Fraction volume : 5 ml. ○ MYP-2 ; ⓘ MYP-7

Table 3. Distribution of molecular weight of modified yeast protein.

Sample	Distribution of molecular weight (%)			
	> 200,000	200,000-100,000	100,000-25,000	(25,000
Yeast protein	64.75	14.26	10.48	10.52
MYP-2	29.07	25.22	20.43	25.27
MYP-7	32.45	20.54	18.74	28.22
Milk casein	40.32	39.97	15.60	4.12

Properties of the binder of CMC, milk casein and modified yeast protein for coated paper

The sheet properties and printabilities of papers coated with modified yeast proteins to which CMC or milk casein was added, were measured under conditions as shown in Table 4. It was obvious that the brightness, gloss, smoothness of the sheet properties or gloss of printability were as good as that of milk casein, the same results with A, B, C or D modified yeast protein in previous paper (Khai et *al.*, 1974). But the IGT pick resistance in this paper show-

Table 4. Properties of the binder of CMC, milk casein adding modified yeast protein for coated paper.

Sample	IYP-2 : Milk casein(10 : 5)	MYP-2: CMC (14.5 : 0.5)	Starch	Milk casein	A modified* yeast protein
Binder/SBR Latex Rati	10/10	10/10	110/10	10/10	10/10
UW-90 (Kaolin Clay)	100	100	3.00	100	100
Solid Content (%)	40	40	40	40	40
pH	9.8	9.7	7.0	9.8	9.3
Coatings (g/cm^2)	1.5.3	16.6	20.1	20.0	16.5
IGT pick resistance	155	114	196	238	111
Wet pick resistance	3.3	3.6	1.8	3.5	1.0
Wet rub resistance	13	11	2	12	8.0
Gloss (%)	82.6	82.4	89.9	84.7	75.1
Ink set	2.8	2.5	1.8	2.8	4.5
Ink Transfer	3.3	3.0	1.8	2.8	4.5

* A modified yeast protein: in previous paper.

Conditions of experiment

1. Coating color : Binder/Pigment=20/100
2. Solubility : NH_4OH ; 10% concentration to modified yeast protein and casein.
3. Dispersion reagent : Sodium Hexametaphosphate ; 0.3 % concentration to pigments.
4. Coating : Coating method : The application for coated paper. Dry temperature ; room temperature.
5. Calender : Pressure; 20 Kg/cm^2. Temperature; 70°C
6. Printability : Gloss: Hunter ; 75°-75° Gloss. Speed Kind Ace P-90 Red Ink. IGT pick resistance: FINE INK (T. V.=18) made in DAINIPPON INK CP., LTD. Ink set : Dry Speed of Ink on Coated paper. Speed King Ace 12 Scarlet Ink; 0.3 ml. Ink transfer : Ink for photography.
7. Sheet properties : Wet pick resistance : Wet pick resistance of the surface of coated paper. Wet rub resistance: The method rubbed with finger. Judgement; the averable of 5 times.

ed a little improvement of the sample of MYP-2 (mixture of 2 hrs modified yeast protein 10% and milk casein 5%), compared with that of A, B. C or D modified yeast protein, however not so good as milk casein, while wet pick resistance and wet rub resistance, especially wet pick resistance improved very much from 1.5 in the A, B, C and D modified yeast protein to 3.6, very near to that of milk casein, and the wet rub resistance was 7-10, in this time, it becomes 10-13.

DISCUSSION

Coated paper, which is also termed glazed, enameled or art paper, was developed to satisfy the demands of printers for a paped upon which fine halftones could be reproduced with good results. Such paper is prepared by mixing mineral materials with a solution of an adhesive and applying this mixture in a thin, even layer to the surface of an ordinary sheet of paper. The function of the adhesive is to bind the mineral materials so firmly to the paper that it will not be removed or "picked" off during the printing operation, while the mineral materials form a surface which is receptive to ink. Such a coating covers the individual fibers on the surface of the paper and also fills any hollows between them, so that the paper, after calendering, has a smooth, even and continuous surface, which permits the finest dots of the half-tone plates to be reproduced perfectly. But in the previous paper, the ammonia-modified yeast protein solution presented a strong thixotropic flow like that of the modified yeast protein in this paper it may cause an ununiformity when mixing modified yeast protein with mineral materials. Thus, the flow curve of modified yeast protein has to vary as close as possible to Newtonian or weak thixotropic flow. Again, from the data (Tanaka *et al.*, 1967) reported that the paper surface sized by CMC, showed such characteristics as high oil and air resistance and high wet tensile strength. Therefore, in order to improve the wet pick, wet rub or IGT pick resistance, CMC, MC, sodium arginate or milk casein was used to vary the properties of the modified yeast protein. The results in Fig. 3 show that the 8 hrs or 10 hrs modified yeast protein takes on an enhanced effect with CMC, MC, or sodium arginate, although added in a small amount of CMC or sodium arginate such as 0.5% compared with 14.5% modified yeast protein, transformed the modified yeast protein flow curve from weak thixotropic to strong thixotropic. Although, this mixture has a good effect on improving the printability, it is very difficult to maintain a uniformity when mixing with mineral materials. In the case of milk casein addition (5 % milk casein : 10 % modified yeast protein), the flow curve of 2 hrs modified yeast protein could be improved and makes the flow nearer to that of milk casein. The printability such as IGT pick resistance, wet pick resistance or wet rub resistance also improved as shown in Table 4, the loss caused by acid-unprecipitation of 2 hrs modification was 23 % compared with 4 hrs modification was 24.5%, and 10 hrs modification was 28.5%. From the data in Figs. 3-6, it is obvious that, the interaction of the polar groups occurred in the modified yeast protein-ammonia solution when standing at room temperature for a time, was more rapid than that of milk casein, although in the state of same or smaller viscosity than milk casein. The degree of this interaction increased rapidly with the increase of concentration of modified yeast protein, while milk casein increased a little, caused no variation in the flow curve. Therefore, in the high concentration (15%), modified yeast protein *molecules* reacted together a lot and could not bind uniformly with mineral materials, but when modified yeast protein concentration decreased to 10% and mixed with 5% milk casein, the flow curve of the mixture shows a weak thixotropic flow, gives a good uniformity when mixing

with mineral materials, the printabilities were also improved. Again, as shown in Fig. **5,** the **2** hrs modified yeast protein when mixed with milk casein **(10: 5)** showed a weak thixotropic flow, but when the paper coater reached a high speed, over **80** rpm, the flow tends to Newtonian flow, and the viscosity rapidly decreased. This property was very appropriate for the coating machine, especially with a roll coater, rather than a brush or air knife coater (Murai *et al.*, 1964 ; Muramoto, 1960; Bain *et al.,* 1961).

Finally, from the above results, it is clear that the **2** hrs modified yeast protein obtained by this method is good in storage, purity, color and very transparent when dissolved in alkali solution, especially when milk casein is added, showed not only the flow behaviors, but also the IGT pick, wet pick or wet rub resistance could be improved. Therefore, this modified yeast protein obtained from this method is good enough to be used for mass-production and applying paper coating.

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