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A Comparison of Insolubilizers for NaOH Cut Protein Coatings

Jon Rock
Western Michigan University

A COMPARISON OF INSOLUBILIZERS FOR NaOH CUT PROTEIN COATINGS

by
Jon Rock

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ABSTRACT

Soy protein is commonly dispersed with NH_4OH, which is a volatile alkali driven off during the drying process. This creates a potential health hazard. Sodium hydroxide, which does not vaporize, can be used to disperse the protein. However, when using it, it is diffficult to develop water resistance. This project is designed to find an additive that when used in conjunction with NaOH dispersed proteins will produce a water resistant coating.

Four insolubilizing agents: melamine formaldehyde, ammonium zirconium carbonate, glyoxal, and sunrez 700FF, were tested with 2.5-3.5 and 5% NaOH dispersed proteins, while a 15% NH_4OH dispersed protein was used as a control. The prepared coatings were then tested for variations in pH, viscosity, brightness, dry pick, wet pick and wet rub.

At the levels recommended by the manufacture of the four insolubilizers tested, none produced both wet and dry pick results without a large increase in viscosity.

Coatings insolubilized with glyoxal had an intolerable viscosity increase. Brightness also decreased with its use. However, glyoxal did produce the best wet pick and wet rub resistance when used with the NaOH cut proteins.

The lowest viscosity NaOH dispersed protein coatings were insolubilized with AZC and wet rub resistance increased with increasing levels of this insolubilizer.

Protein dispersed at the 3.5% NaOH level produced the best dry and wet pick results, while the 2.5% NaOH dispersed protein gave the best wet rub results within the NaOH cut proteins.

Because wet rub improved with increased levels of AZC for the NaOH cut

protein coatings, it should be possible to obtain the wet rub results required by increasing the level of AZC.

An alternate solution to the ammonium problem would be to reduce its level rather than eliminating it completely. This might be accomplished by using a combination of NaOH and NH_4OH to disperse the protein.

TABLE OF CONTENTS

TABLE OF CONTENTS

(Cont.)

INTRODUCTION

Soy protein is commonly used as part of the binding system in board coatings because it provides glueability, stiffness and can be made highly water resistant, more so than common starch coatings. Currently, soy protein is dissolved with NH_4OH which vaporizes when the coating is dried. This creates a potential health hazard because the ammonium ends up in the atmosphere.

Various nonvolatile alkalis can be used to cut protein. However, NaOH was chosen because it produces a strong protein film, and is commonly used for other mill processes. The problem stems from the fact that nonvolatile alkalis leave salts or residues which neutralize or stop the insolubilization reaction, thus making it difficult to develop good H_2O resistance. It is the intention of this project to test various insolubilizers with NaOH cut proteins to find a system which could be substituted for the conventional NH_4OH cut protein.

NaOH cut protein will be tested with four insolubilizers and compared to a NH_4OH cut protein control. These clay coatings will then be tested for variations in dry pick, wet pick, wet rub, and brightness. This data will then be examined to determine which system would operate best in the offset lithography process.

THEORETICAL DISCUSSION

Health Effects

Ammonia is a volatile H_2O soluble alkali which is an irritant that affects the skin, eyes, mucous membrane of the upper respiratory tract, and lungs.[1] The effects of ammonia on human health can result from accidental acute toxic exposure, from chronic exposure to low concentrations in the work place or as an air pollutant.[1] The degree and manifestation of dysfunction and tissue damage depend on the concentration, duration and type of exposure. Accidental release of high concentrations of ammonia from faulty valve connections, containers, and handling by workers in industry and agriculture results in numerous deaths and injuries each year.[1]

Of all the alkalies, NH_4OH causes the deepest damage to the eyes.[1] The rapidity of corneal penetration by ammonia was demonstrated by Siegrist, who detected ammonia in the interior chamber five seconds after topical application. Ammonia, therefore, tends to cause more corneal, endothelial damage, stromal edema, iritis, and lens damage than other alkalis.[1] NaOH could be used in solid form, thus eliminating this danger to workers in the coating formulation area.

A number of studies have been reported on the adverse effects of chronic low-concentration exposure to ammonia on man. However, most of these reports have delt with chronic exposure to a mixture of irritating air pollutants, such as nitrogen oxides, sulfur dioxide, and ammonia. Currently the U. S. Federal Standard for exposure to ammonia is 50 ppm over an eight hour time weighted average.[1] Therefore, it is possible that OSHA requirements could be tightened.

Coating Properties

Data from Tappi Monograph 22 shows that dry pick (Dennison Wax Pick) for NaOH cut coatings is comparable to those cut with NH_4OH.[2] The wet rub properties, however, are superior for the NH_4OH cut coatings.

SYNTHETIC AND PROTEIN ADHESIVES

EFFECT OF AMOUNT AND TYPE OF ALKALI

Type and percentage of alkali used to disperse protein from which clay coating mixes were prepared	Clay coating mix viscosity in centipoises at 30°C.	Clay coating mix pH at 30°C.	Adhesive strength (Dennison waxes)	Wet abrasion resistance, 14 day aging (mg./wc.)*
NH_4OH				
4.5	372	7.24	3.8	0.76
7.5	355	8.45	4.6	0.30
10.0	340	8.77	4.2	0.52
12.5	330	8.95	5.0	0.62
15.0	325	9.08	4.9	0.58
NaOH				
2.0	670	6.58	2.9	1.82
2.5	584	7.00	3.3	2.48
3.0	528	7.72	4.5	3.32
3.5	548	8.60	4.8	3.44
4.0	492	9.12	4.6	4.34
Borax				
15.0	490	7.52	4.0	3.26
20.0	631	7.85	5.1	4.36
25.0	600	8.08	4.8	5.28
30.0	650	8.18	5.2	5.14
35.0	645	8.51	5.5	6.16

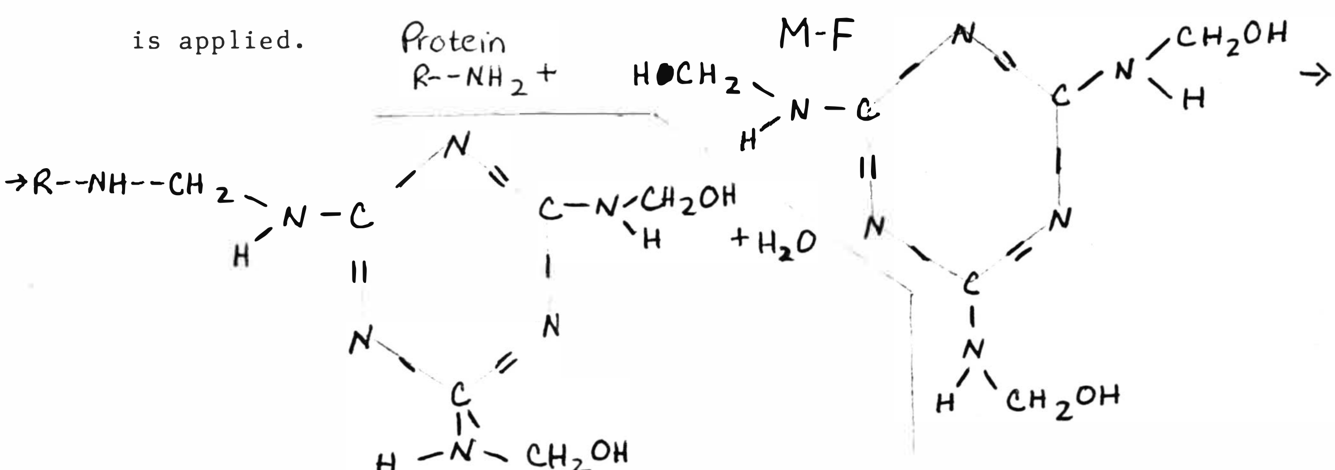
* Milligrams of coating removed per wear cycle on the Taber abrasion instrument.

Coatings require wet strength to operate efficiently on lithographic presses where the repellancy of ink and water are used to transfer the image. Three problems which result from weak coatings are pickout, hickies, and scumming. Pickout is a defect in the finished sheet. Holes are formed on the sheet surface when a portion of the coating is picked off due to the tack force of the ink. This, in turn, sticks to the printing blanket causing hickies or localized areas of poor ink transfer in the image area. If the coating makes its way into the fountain solution (pH 3.5-5) the acid balance is upset and scumming results, which is a light ink film in the non-image area. The probability of coating failure is increased in multicolor printing operations where the surface may be softened by several successive applications of moisture.

Protein cut with NaOH exhibits higher viscosities than those cut with NH_4OH. The increase in viscosity can be a benefit if penetration of the adhesive into the base sheet has to be reduced. Lower coating solids level could also be used to reduce viscosity. Sodium hydroxide also requires very close control in preparing the protein dispersion for an excess of alkali or high cooking temperatures can lead to loss in strength through over-hydrolysis of the soy protein.[3] However, if the concentration of the protein in water and the cutting temperature are held constant, a control for the correct amount of alkali can be based on pH tests made at a constant temperature ($30^{o}C$).[2]

Insolubilizing Agents

Melamine Formaldehyde. There are many types of coating insolubilizers. However, the most commonly used are the formaldehyde donors. These resins work by cross linking with themselves, and blocking water reactive sites. Reduced water sensitivity is obtained by the reaction of formaldehyde with free amino groups forming methylene bridges.[3] Two chains of macromolecules link together $R - NH_2 + H_2CO + H_2N - R$ to form $R - NH - CH_2 - NH - R + H_2O$. Urea formaldehyde and melamine formaldehyde are the two work horses in this group. Melamine formaldehyde has more bonding sites, and does not exhibit the viscosity increase with protein which is characteristic of urea-formaldehyde. Curing of the M-F resin is also less pH sensitive. Both resins require heat to cure and will continue to cure for weeks after the coating is applied.



Glyoxal

Glyoxal, a dialdehyde is another commonly used insolubilizer.[4] This resin attains most of its final strength immediately after being dried. Glyoxal affects little change in paper other than producing wet strength. The absorbency and "hand" remain essentially the same. In contrast, paper treated with urea and melamine formaldehyde resins to the same level are noticeably less absorbent and tend to have a harsher "hand". This quality makes glyoxal-treated papers especially useful for towels, tissue, and toilet paper. Glyoxal works best in a pH range of six to eight. If made alkaline, glyoxal undergoes an internal cannizzaro reaction in which it slowly forms salts of glycolic acid. Glyoxal is generally more effecient than typical urea and melamine resins.[5] Glyoxal in solution form is an effective insolubilizing agent for soy protein coatings but cannot be used in white or light-colored coatings because of its darking effect on the protein.[3]

Ammonium Zirconium Carbonate

Ammonium zirconium carbonate (known as AZC) and the temperature stabilized version Bacote 20 have recently received Federal Drug Administration approval as components of paper and paperboard in contact with aqueous and fatty foods.

AZC reacts with proteinaceous materials on drying and gives insolubilization at high pHs. The reaction occurs between AZC and the amino hydroxyl or carboxyl groups on the protein as water is removed. Therefore, a sheet insolubilized with AZC should give maximum water resistance immediately after leaving the dryer. AZC has other potential advantages over conventional insolubilizing agents. The solution will react with protein even though non-volatile soluble alkalies such as NaOH or soda ash are used for dispersion. When dried, AZC forms a white slightly carbonated zirconium hydroxide which

When dried, AZC forms a white slightly carbonated zirconium hydroxide which has a high refractance in a wide spectral range. Therefore, there is no loss in brightness, or opacity which sometimes accompanies organic insolubilizers.[6]

Sunrez 700FF

Recently formaldehyde has received considerable attention due to fumes produced by formaldehyde foam insulation. Many insolubilizers used today produce formaldehyde fumes. Therefore, to eliminate this hazard, a formaldehyde free insolubilizer produced by Sun Chemical Corporation will be tested. Sunrez 700Ff claims to provide excellent wet rub and wet pick resistance to pigmented coatings.[7]

EXPERIMENTAL PROCEDURE

I Chemicals

1. Pro-Cote 200, (Ralston Purina Company) 91.5% solids O.D.
2. NH_4H 28%
3. NaOH 50%
4. AZC, Bacote 20 (Magnesium Election Ltd.) 20% solids O.D.
5. Glyoxal, Parez 801 (American Cyanamid Company) 40% solids O.D.
6. Melamine Formaldehyde, Parez 616 (American Cyanamid Company) 80% solids O.D.
7. Sunrez 700 FF (Sun Chemical Corporation) 45% solids O.D.
8. TiO_2, Tri-Pure (Dupont Corporation) 73.5% solids O.D.
9. Hydrafine (J.M. Huber Company) 70% solids O.D.
10. Calgon T
11. Distilled H_2O

II Instruments and Materials

1. Power Stat (variac)
2. Centrifuge
3. $105^{o}C$ Convection Oven
4. pH Meter
5. Drawdown Rod 16#
6. Balance
7. Sample Bottles
8. Heating Sock
9. Ring Stand
10. Fisher Dyna-Mix
11. Timer
12. Thermometer
13. Drying Dishes
14. Brookfield Viscometer
15. Turbidimeter
16. Calender Stack
17. Brightness Meter
18. IGT Printability Tester
19. Cowels Dissolver
20. Small Paint Brush
21. Multilith Pads
22. 68.9 g/m^2 Raw Stock
23. AB Dick Offset Roller Cleaner and Blanket Wash

Coating Preparations

Protein Cooking Procedure. 1. Heat 600 ml of distilled (or deionized) H_2O in a 800 ml beaker to 140^oF (60^oC).

2. Set the Bunn Warmer so that the highest temperature is 140^oF (60^oC).

3. Pour about 197 ml H_2O into a 600 ml beaker.

4. Put the 600 ml beaker in the Bunn Warmer and lower the lightning mixer so that the propeller is just off the bottom of the beaker (maintain temperature in beaker at 58^oC).

5. Set lightnin mixer at approximately 390 rpm. Add 36 g of the Pro-Cote and allow it to wet out for one minute.

6. Add 6 ml of 28% NH_4OH (about 15% of the Pro-Cote).

7. Cover and allow to mix at 140^oF (60^oC) for 30 minutes.

8. Cool to room temperature (70^oF) for determination of viscosity, pH, and percentage solids.

Coating Make-up Procedure. 1. Dissolve .5% Calgon T (based on A.D. weight of clay) in H_2O.

2. While agitating clay with Cowles Dissolver, slowly add H_2O, then mix for 20 minutes.

3. Allow all coating components to cool to room temperature.

4. Weigh out the required amount of cut protein in 400 ml beaker.

5. Add specified amount of clay and TiO_2 slurries to the protein.

6. After pipetting the correct amount of insolubilizer, add H_2O to obtain the percentage solids desired.

7. Mix components for three minutes using the Fisher-Dyna-Mixer at setting 5.

8. Determine pH and viscosity immediately after blending the components 72^oF.

9. Add 10 grams of coating to a drying pan for determination of percent solids.

Application and Conditioning. The 14 x 10 inch sheets of raw stock used for coating had an uncoated brightness of 72.4 and basis weight of 68.92 g/m^2. A number 16 drawdown rod was used to make three samples of each coating. The average coat weight being 32.5 g/m^2.

All coatings were allowed to air dry before being oven dried at 105^oC for five minutes. Cold supercalendering was used to improve the uniformity of the sheet surface. Each sheet received four nips at 30 psi four days after being coated. All samples were then stored at constant temperature and humidity conditions until tested.

Testing Procedure

Dry Pick. The coatings were conditioned at constant temperature and humidity for five days prior to testing. An IGT printability tester was used with low viscosity oil at speeds of 1, 2, and 3 m/sec. depending on the coating strength. The failure rating was assigned the value where two pick outs occured within one increment of the rating scale. Two to six tests were run on each sheet, depending upon reproducibility. These values were then averaged.

Wet Pick. Coatings for the wet pick test were conditioned at constant temperature and humidity for seven days prior to being tested. The IGT printability tester and low viscosity oil were identical to those described in the dry pick procedure. Multilith pads, weighing 2.4 grams, were folded in half twice, then damped with distilled H_2O until the total weight was nine grams. After a uniform film of oil covered the Westvaco roll and the 1.5 inch sample was in place, the damp pad was wiped across the coating surface at a uniform speed. Five seconds after the moisture was applied, the pick test was run. Because the wet pick values were low, the failure rating was assigned to the first major picking area. Two to six tests were run on each coating, depending upon reproducibility. These values were then averaged.

Wet Rub. The wet test was run after 14 days of conditioning at constant temperature and humidity. A Hach model 2100A turbidimeter was used to rate the relative degree of coating insolubilization.

1. Draw a one inch diamater circle on the coated sheet being tested.

2. Using an eye droper, add three drops of distilled water to the circle.

3. After waiting five seconds, make 15 revolutions inside the circle with the index finger using light pressure.

4. Wipe finger off with damp brush. Then use dampened brush to wipe solubilized coating out of the circle in one pass.

5. Wash the removed coating out of the brush and into a 50 ml beaker with 30 ml. of water.

6. Calibrate the turbidity meter with the 100 NTU standard.

7. Pour the 30 ml of coating water mixture into the turbudity sample tube.

8. Make measurements using the 100 NTU or 1000 NTU scale. Recalibrate for each scale.

9. After washing the brush, wipe excess water off identically each time to insure a constant brush dampness.

RESULTS

Protein Properties

The viscosities for each of the four dissolved protein dispersions were below 100 centipoise. The viscosity of the NH_4OH cut protein was lower than the (2.5 and 3.5) percentage. NaOH cut proteins but higher than the 5% NaOH cut protein.

The pH of the protein increased with increasing levels of NaOH which would be expected.

A sample of each protein was centrifuged for 45 minutes to determine what percentage of the cut protein was left undissolved. The 2.5% NaOH cut protein remained cloudy after being centrifuged and had the least amount of sediment (see Table I).

Wet Coating Properties

Glyoxal had the largest effect on viscosity. The viscosity increase was proportional to the amount of NaOH used to cut the protein. AZC produced the lowest viscosity NaOH cut protein coatings.

Coating viscosity decreased as the amount of NaOH increased with all insolubilizers except glyoxal.

Only the 5% NaOH cut protein coatings approach the viscosity produced when NH_4OH is used to disperse the protein.

Percentage insolubilizer throughout this paper is equal to the amount specified by the manufacture and can be found in the Table II key.

Coating Properties

Brightness. The NaOH level used to cut the protein did effect the final coating brightness. As the level of NaOH increased the coating brightness

TABLE I

COOKED PROTEIN PROPERTIES

	15 NH_4OH A	2.5% NaOH B	3.5% NaOH C	5.0% NaOH D
% Solids	14.2	14.3	14.3	14.3
Viscosity 100 rpm Centipoise 70°F	70	85	90	60
Ph 70°F	9.75	8.8	10.5	12
% Residual ml	Total = 4 x = 3.9 y = .1	Total = .8 x = .8 y = 0.0	Total = 8 x = 2.7 y = .2	Total = 3 x = 3.95 y = .05

Key:

1. % Residual - Samples were centrifuged for 45 minutes at high speed. Each tube contained 40 ml total cut protein.

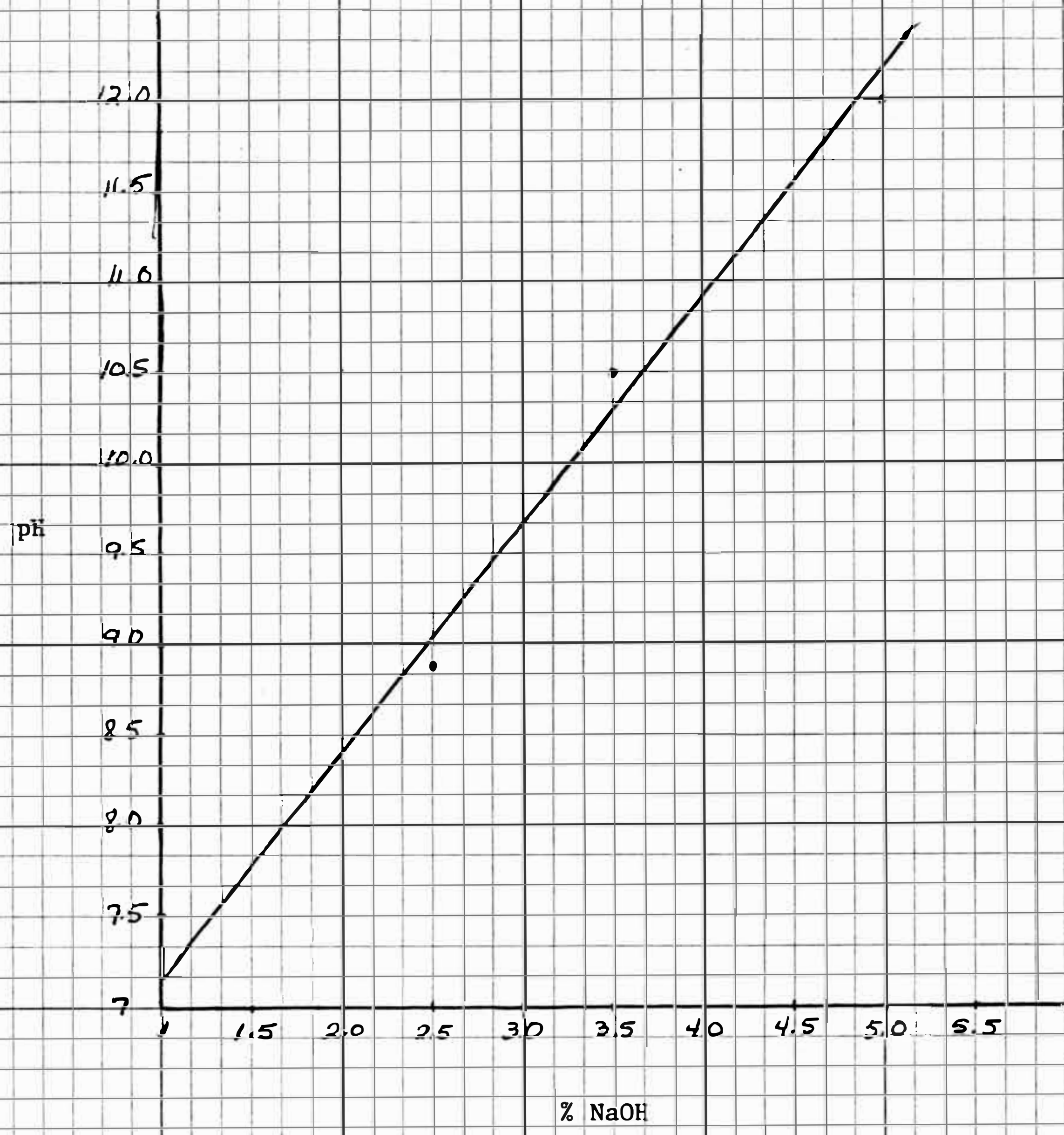
2. % Solids - 10 grams of each protein were dried at 105°C in weighing dishes. Two samples of each protein were then weighed and averaged.

3. Viscosity and pH - Samples were agitated before the measurement was taken at 70°F.

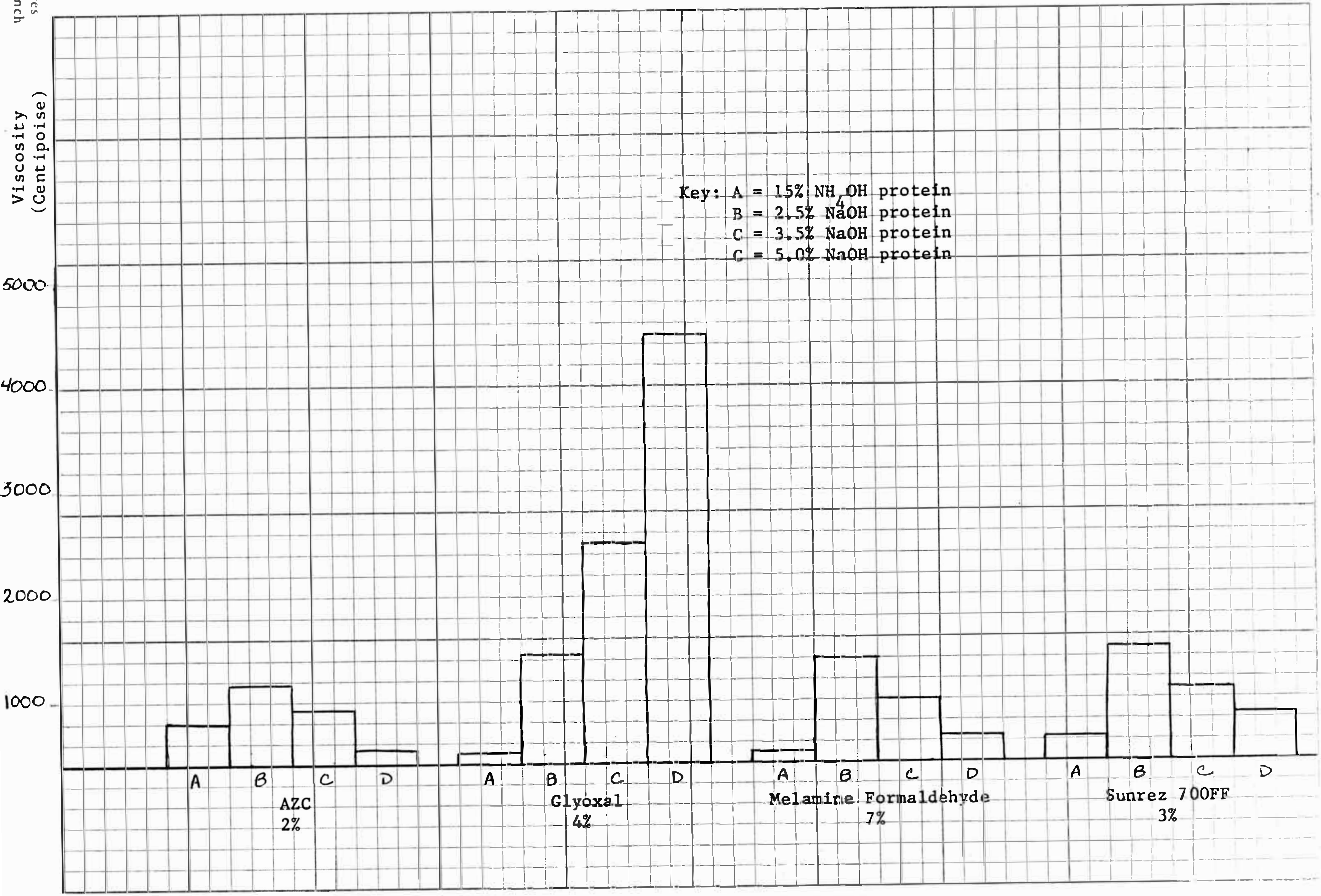
4. Protein used - Pro-Cote 200 (Ralson Purina Co.). Air dry = (91.5% Solids) = as received protein.

5. % Cutting Alkali was based on the air dry weight of protein.

6. 50% NaOH was used in all NaOH cut coatings.



% NaOH vs. PROTEIN pH
Figure 1



COATING INSOLUBILIZERS vs.VISCOSITY
Figure 2

TABLE II

COATING PROPERTIES

Coating Number		15% NH_4OH A	2.5% NaOH B	3.5% NaOH C	5% NaOH D
Viscosity 100 rpm CPS.					
	1	530	1200	880	570
AZC	2	600	1150	900	540
	3	575	1000	740	515
	4	540	1220	2280	2520
Glyoxal	5	500	1440	2520	4500
	6	630	1480	2320	2960
	7	615	1360	1080	600
MF	8	525	1400	1000	640
	9	510	1320	1100	620
	10	550	1260	1200	730
700FF	11	605	1480	1120	820
	12	610	1300	1140	790
pH at $72^{O}F$					
	1	9.4	8.75	9.5	10.3
AZC	2	9.42	8.9	9.4	10.0
	3	9.35	9	9.35	9.8
	4	9.3	8.4	9.35	10.2
Glyoxal	5	8.9	8.15	9.1	9.85
	6	8.6	8	9.0	10.0
	7	9.5	8.6	9.8	10.65
MF	8	9.5	8.6	9.75	10.7
	9	9.5	8.6	9.78	10.7
	10	9.5	8.6	9.75	10.65
700FF	11	9.5	8.65	9.75	10.65
	12	9.45	8.7	9.75	10.4
% Solids					
	1	45.0	45.0	44.8	44.8
AZC	2	44.5	44.0	44.9	44.5
	3	44.5	44.0	44.5	45
	4	44.5	44.0	43.8	44.0
Glyoxal	5	44.5	44.5	44.0	45.0
	6	44.0	44.0	44.0	44.8
	7	44.0	43.5	44	45
MF	8	44.5	44	44	45
	9	44.0	43	44	44.5
	10	45.0	44	45	45
700FF	11	44.0	44.5	44.6	45
	12	45.0	44	44	45

TABLE II

(Key)

1. AZC BaCote (20% Solids), (.75-2-3.5)% AZC solution as received based on the total coating pigment was used.

Coating #1 = .75% AZC
#2 = 2.0% AZC
#3 = 3.5% AZC

2. Glyoxal Parez 801 (40% Solids), (2-4-6)% Glyoxal resin solids based on the as received weight of the protein were used.

Coating #4 = 2% Glyoxal
#5 = 4% Glyoxal
#6 = 6% Glyoxal

3. Melamine Formaldehyde Parez 616 (80% Solids), (5-7-10)% Melamine resin solids based on the as received weight of the protein.

Coating #7 = 5% Malamine
#8 = 7% Melamine
#9 = 10% Melamine

4. Sun Rez 700FF (45% Solids) (2-3-4)% 700FF resin solids based on the as received weight of the protein.

Coating #10 = 2% Sun Rez 700FF
#11 = 3% Sun Rez 700FF
#12 = 4% Sun Rez 700FF

5. The amount of each insolubilizer was based on the manufacturer's recommended level.

6. All pH's were measured after standardizing using the pH 10 buffer, and at $72^{o}F$. The measurement was made immediately after the coating was mixed.

7. Brookfield viscosity was determined immediately after mixing the coating at $72^{o}F$ and 100 rpm.

8. TiO_2 used was Dupont Tri-Pure Slurry RP-S 73.5% Solids.

9. Clay used was Hydrafine 70% Solids pH = 7.75 dispersed with .5% Calgon T.

10. The coatings were mixed for three minutes with the Fisher Dyna Mixer on setting 5.

11. % Solids - one 10 gram sample of each coating was dried at $105^{o}C$ overnight to determine the solids level.

TABLE III

BRIGHTNESS AND COAT WEIGHT

		15% NH_4OH A	2.5% NaOH B	3.5% NaOH C	5% NaOH D
Brightness					
	1	79.4	81	79.4	78.8
AZC	2	80.4	80.3	79.8	79.1
	3	79.8	79.4	79.9	80.1
	4	79.3	78.3	77.3	76.2
Glyoxal	5	79.6	77.9	77.2	76.9
	6	79.3	78.8	76.6	75.8
	7	81	80.9	78.7	78.4
MF	8	80.1	80.3	78.6	79.0
	9	80.4	80.5	79.0	78.4
	10	81.7	80.8	79.4	78.2
700FF	11	80.6	80.5	79.0	78.5
	12	79.6	81.7	80.2	80.6
Coat Weight g/m^2					
	1	23.6	30.9	24.3	23.2
AZC	2	51.4	57.2	37.4	32.5
	3	28.9	62.12	21.5	31.4
	4	50.3	22.1	26.0	22.6
Glyoxal	5	28.4	25.4	22.1	26.4
	6	29.22	23.2	22.2	27.0
	7	48.4	22.1	22.1	24.8
MF	8	59.9	22.1	30.3	29.7
	9	23.2	37.4	34.2	22.1
	10	28.7	22.6	24.3	22.0
700FF	11	53.3	22.3	24.8	41.8
	12	49.0	22.1	31.9	34.2

Key:

1. Brightness meter calibrated with 77.6 MgO_2 stone.

2. Raw stock brightness = 72.7

3. Coat weight determined from 6" diameter circle.
Raw stock weight = averaged weight in grams x 54.83 = g/m^2

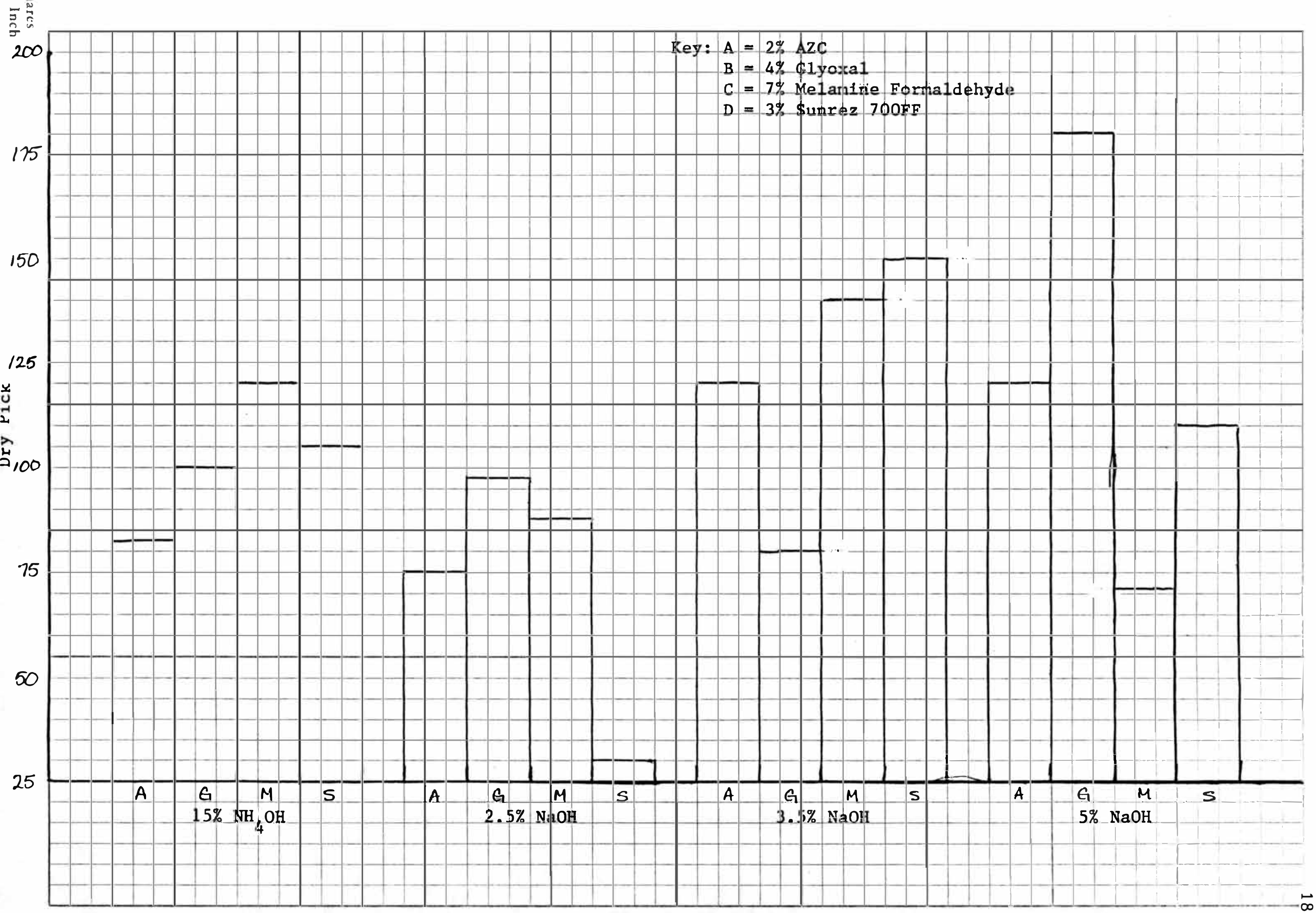
$$= \frac{1.255 + 1.243 + 1.279 + 1.254}{4} \text{ g} \times 54.83$$

$$= 1.257 \text{ g} \times 54.83 = 68.92 \text{ g/m}^2$$

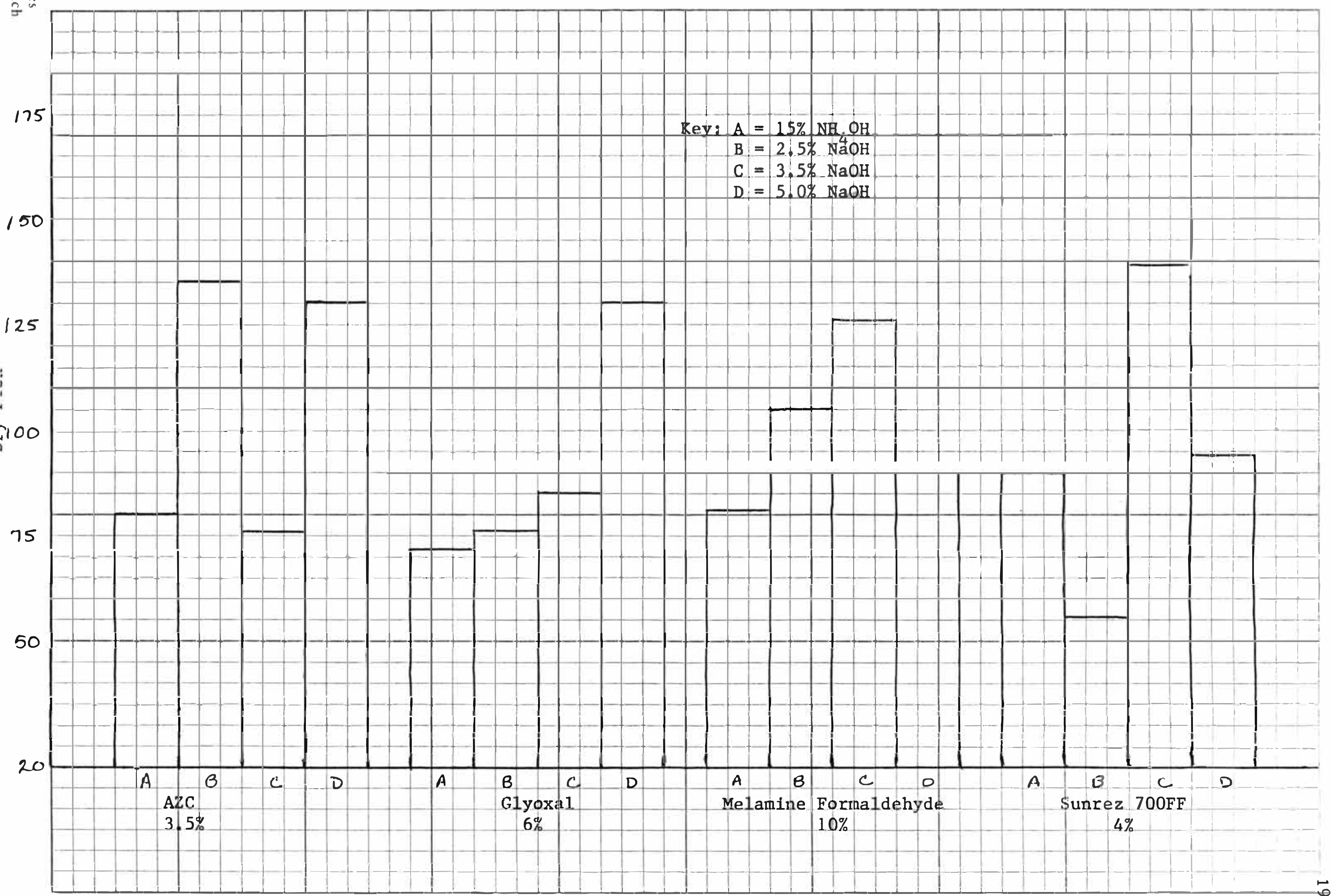
Raw stock weight = 68.92 g/m^2

4. Coat weight = Coated sheet weight - Raw stock = g/m^2 one coat weight was determined for each of the 48 formulations.

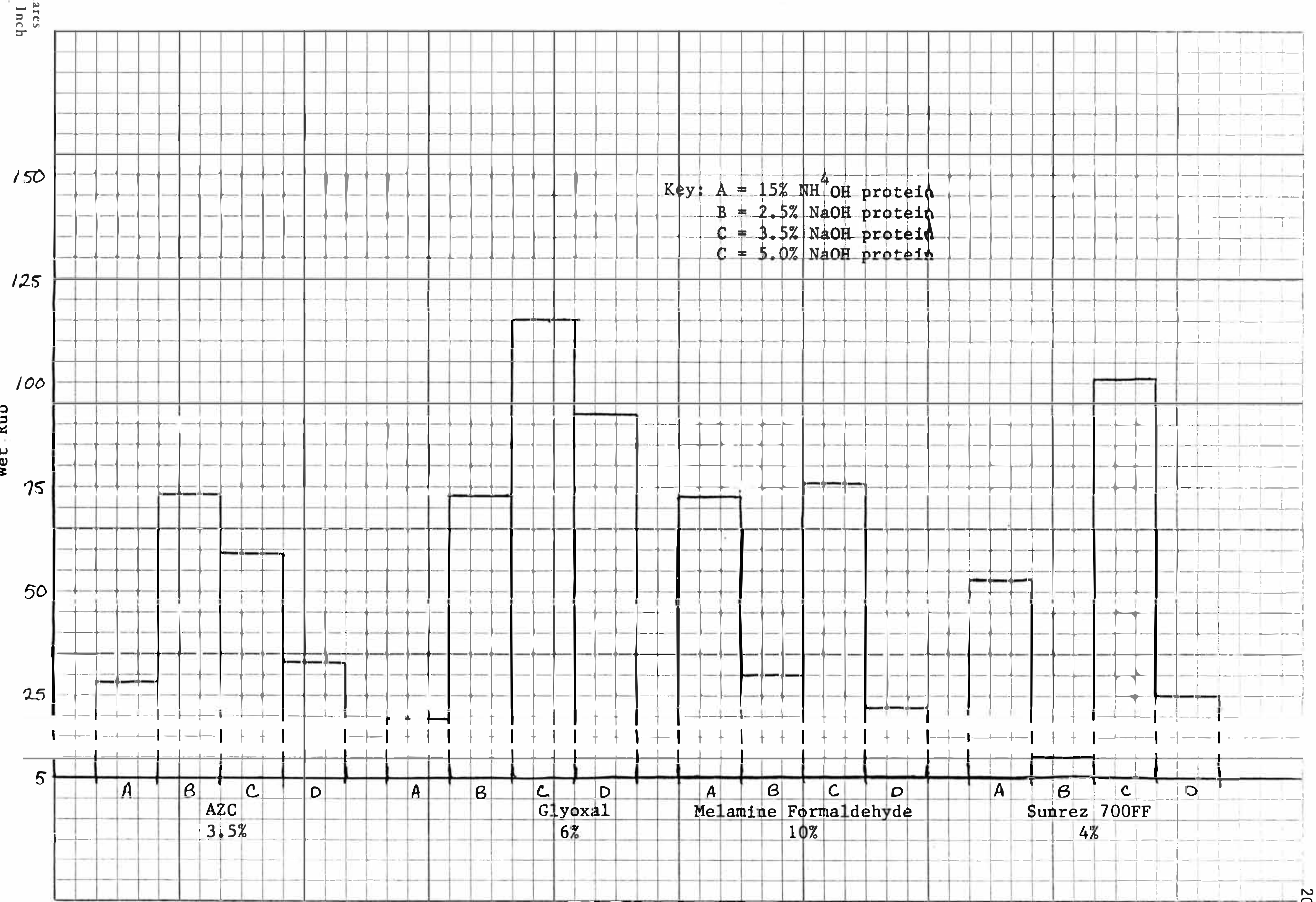
5. Brightness meter used was a Technidyne Corporation S-4 Brightness tester and colorimeter.



DRY PICK OF COATINGS
Figure 3



DRY PICK OF COATINGS GROUPED BY INSOLUBILIZER
Figure 4



WET PICK OF COATINGS

Figure 5

TABLE IV

DRY PICK AND WET PICK RESULTS

		15% NH_4OH A	2.5% NaOH B	3.5%NaOH C	5% NaOH D
5 Day Dry Pick					
	1	90	47	120	133
AZC	2	83	75	120	120
	3	80	137	77	130
	4	105	120	95	117
Glyoxal	5	100	98	80	180
	6	73	77	85	130
	7	97	63	160	115
MF	8	120	88	140	72
	9	82	110	126	93
	10	80	44	135	118
700FF	11	105	30	150	110
	12	90	56	130	94
7 Day Wet Pick					
	1	25	14	46	39*
AZC	2	18	63	50	35*
	3	28	73	58	33*
	4	40	108	78	80
Glyoxal	5	57	97	103	90
	6	19	73	115	93
	7	64	20	69	42*
MF	8	45	30	85	19*
	9	74	30	76	23*
	10	70	13	100	33*
700FF	11	33	10	90	45*
	12	53	10	106	25*

Key:

1. 5 Day Dry Pick - These coatings were conditioned for five days at constant temperature and humidity prior to being tested.

2. An IGT printability tester was used at speeds of 1, 2, and 3m/sec. The oil used was IGT pick-test oil of low viscosity (1500 cps).

3. The failure rating was given at the point where two pick outs occured within one increment of the rating scale.

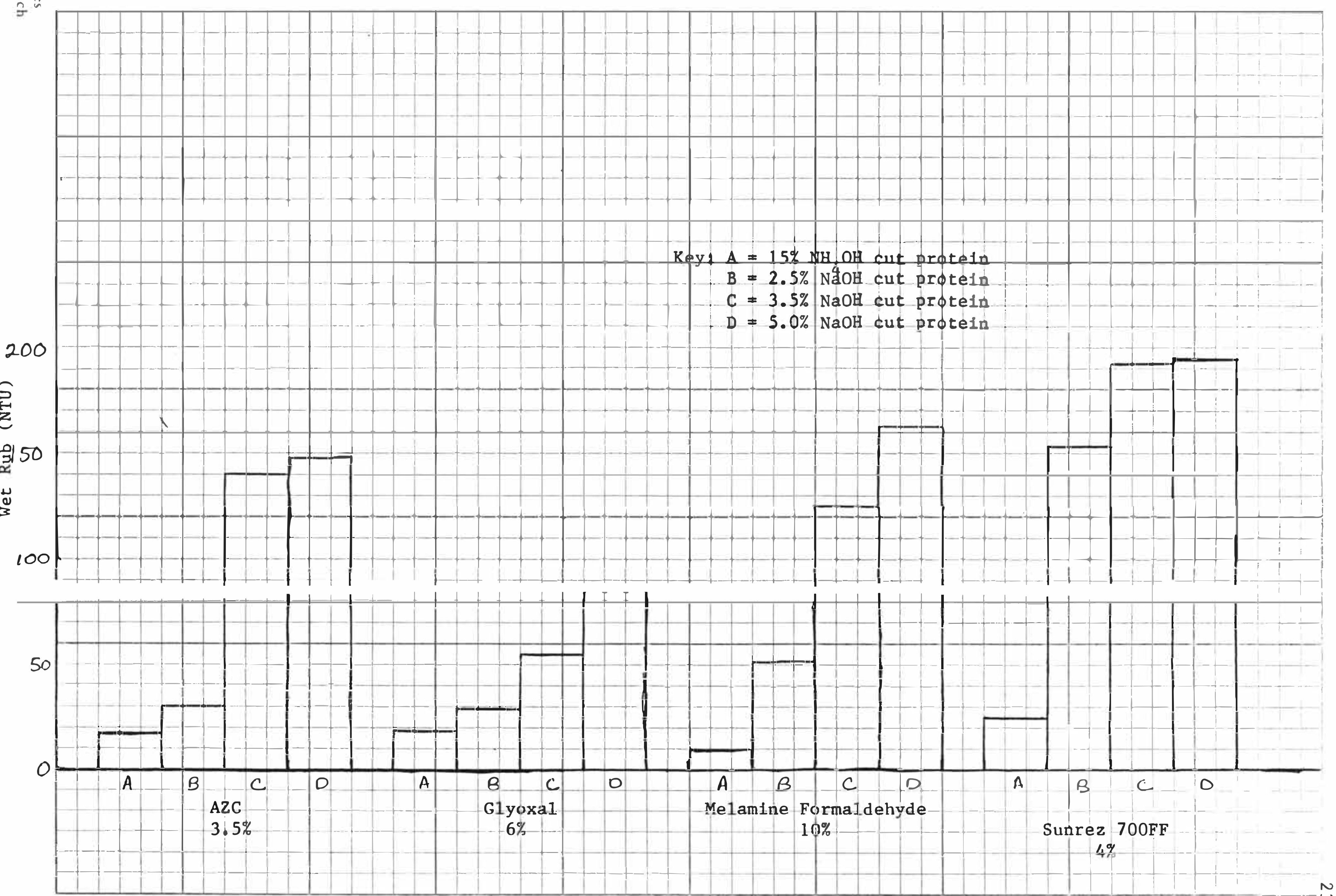
4. 7 Day Wet Pick - These coatings were conditioned for seven days at constant temperature and humidity prior to being tested. The tester, oil and rating system is identical to the 5 Day Dry Pick.

TABLE IV

(Cont.)

5. Each sample was dampened with a multilith pad then run after five seconds.

6. *The coatings formulated with 5% NaOH protein were so soluble a portion of the surface would wipe off when the sample was dampened. Therefore, results for these coatings are questionable.



WET RUB RESULTS
Figure 6

TABLE V

14 DAY WET RUB NTU TURBIDITY UNITS

		15% NH_4OH A	2.5% NaOH B	3.5% NaOH C	5% NaOH D
	1	20	56	165	163
AZC	2	26	46.	190	145
	3	17	30	140	147
	4	19	28	92	100
Glyoxal	5	14	26	64	115
	6	18	28	55	85
	7	15	43	135	200
MF	8	12	55	138	180
	9	10	51	125	163
	10	17	88	155	140
700FF	11	18	143	180	170
	12	25	153	193	195

Key:

1. All coatings condition at constant temperature and humidity for two weeks prior to being tested.

2. Units are Nephelometric Turbidity Units (NTU). A Hach Model 2100A Turbidimeter was used for testing, calibrated with 100NTU standard.

3. Lower reading indicates a higher degree of insolubilization.

decreased for all of the insolubilizers.

The NaOH cut protein coatings insolubilized with glyoxal displayed a slightly lower brightness level than those insolubilizers with other additives at the same NaOH concentration.

The average coat weight for all coatings was 32.5 g/m^2. However, the deviation from this value was larger than expected.

Dry Pick. The 3.5% NaOH cut protein coatings produced the best dry pick results when insolubilized with melamine formaldehyde or sunrez 700FF. The dry pick decreased when the NaOH was increased beyond this level. These coatings also had a higher dry pick than the NH_4OH cut protein coatings insolubilized with the same agents.

The 5% NaOH cut protein produced the best dry pick results using AZC or glyoxal for insolubilization. Most results with the 2.5% NaOH cut protein coatings were poor.

Wet Pick. The wet pick showed a trend similar to the dry pick results. The 3.5% NaOH cut proteins produced the strongest coatings with all insolubilizers except AZC. Glyoxal produced the best wet pick results at each level of NaOH cut protein.

Melamine formaldehyde gave the best results with NH_4OH cut protein coatings, although sunrez 700FF was a close second.

Data from the 5% NaOH cut coatings should be neglected because the coatings began to wash off the raw stock when it was dampened with the multilith pad. This indicates the coating surface may have been too soft to give accurate results.

Wet Rub. As expected, the NH_4OH cut protein coatings produced the best wet rub results. In this group melamine formaldehyde gave the sheet the highest level of wet rub resistance.

Glyoxal gave the highest degree of insolubilization to all the NaOH cut coatings. The 2.5% NaOH coatings approached the NH_4OH coatings when AZC or gloyxal was used as an insolubilizer.

The level of wet rub resistance with AZC was proportional to the amount of insolubilizer added, which wasn't always true of the other insolubilizers. A lower reading on Figure 6 indicates a higher degree of insolubilization.

DISCUSSION OF RESULTS

Cut Proteins

The major increase in viscosity with the NaOH cut protein coatings is produced after the pigments are added to the protein dispersion. Viscosity differences in proteins dispersed with different alkalis was relatively small.

The low sediment level in the centrifuged 2.5% NaOH cut protein might be explained by one of two possibilities. First the sediment may not have consisted of undissolved proteins, or the polymer chains may have been too large, due to lack of sufficient alkali to permit settling of the undissolved fraction. Because the 2.5% cut protein appeared to be cloudy, the second explanation seemed the most logical.

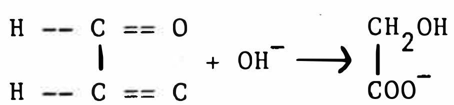
The relationship between the percentage NaOH on the protein and the solution pH appeared to be linear. Therefore, a pH meter could be used to control the level of caustic addition.

Insolubilizers

Glyoxal. The large viscosity increase caused by the addition of glyoxal would prevent its use in NaOH cut protein coatings. This increase may have been caused by the Cannizzaro Reaction, which indicates that if the solution is made alkaline the glyoxal slowly forms salts of glycolic acid.

Glyoxal

(Anhydrous Form)



Cannizzaro Reaction

This assumption seems reasonable because the viscosity increase was proportional to the amount of NaOH in solution.

The brightness reversion characteristic of glyoxal when used in conjunction with protein was also present in the NaOH cut protein coatings.

Glyoxal did provide the NaOH cut coatings with the best wet rub and wet pick resistance.

Melamine Formaldehyde. The melamine formaldehyde resin gave some of the best dry pick results with the 3.5% NaOH cut protein.

In coatings using NH_4OH cut protein the melamine resin produced the best wet pick and wet rub results when added at the 10% level.

AZC. AZC produced the lowest viscosity NaOH cut protein coatings at all levels of caustic addition, and the viscosity usually decreased as the amount of AZC was increased. These viscosities were in the working range of most coating hardware.

The wet pick for the AZC coatings was the pourest of the four insolubilizers tested when NH_4OH or 3.5% NaOH was used to cut the protein. At high levels of addition and 2.5% NaOH cut protein, AZC produced wet rub results which approached the NH_4OH cut coatings. The level of wet rub resistance with AZC usually increased with higher levels of addition which wasn't true of the other additives.

Sunrez 700FF. Sunrez 700FF produced very good dry and wet pick results when used with the 3.5% NaOH cut protein. The data resembled that obtained with the melamine resin. The wet rub, however, was another story. When 2.5% NaOH was used in the binder, the sunrez gave the poorest wet rub results of the four insolubilizers, and wet rub decresed as the level of sunrez increased with all alkalies including NH_4OH.

Alkali Level

For dry and wet pick resistance, the 3.5% NaOH cut protein performed the best often with results higher than those obtained with the NH_4OH cut proteins. This level of caustic seemed ideal for completely cutting the protein without over hydrolizing it.

The 2.5% NaOH level didn't seem to dissolve enough protein to provide adequate picking strength. However, it gave the best wet rub results, due to the lower level of sodium salts left in the coating. It might be possible to cut the protein at a higher temperature with the lower NaOH level. However, a price is paid because higher cooking temperatures produce darker protein dispersions.

CONCLUSIONS

The following conclusions can be made regarding the use of ammonium zirconium carbonate, melamine formaldehyde, glyoxal, and sunrez 700FF as insolubilizers for coatings prepared with NH_4OH and NaOH cut proteins.

Glyoxal

1. Glyoxal produced a large increase in viscosity when used with NaOH cut proteins.

2. Glyoxal reduced coating brightness when formulated with NaOH cut proteins.

3. The best wet rub and wet pick resistance for NaOH cut protein coatings was produced using glyoxal.

Melamine Formaldehyde

1. Some of the best dry pick results with the 3.5% NaOH cut protein coatings were obtained using melamine formaldehyde.

2. In coatings using NH_4OH cut protein, melamine formaldehyde produced the best wet pick and wet rub results when added to a 10% level.

Ammonium Zirconium Carbonate

1. AZC produced the lowest viscosity NaOH cut proteins.

2. Wet pick for AZC coatings was the poorest of four insolubilizers tested when NH_4OH or 3.5% NaOH was used to cut the protein.

3. At high levels of addition with 2.5% NaOH cut protein, AZC produced wet rub results which approached NH_4OH cut coatings.

4. Wet rub resistance increased with increasing levels of AZC.

Sunrez 700FF

1. Sunrez produced good dry and wet pick results when used with 3.5% NaOH cut protein.

2. When 2.5% NaOH cut protein was used, sunrez gave the poorest wet rub results of the four insolubilizers.

3. Wet rub decreased as the level of sunrez increased with all alkalies including NH_4OH.

Alkali Level

1. The 3.5% NaOH cut protein produced the strongest coatings for dry and wet pick.

2. The 2.5% NaOH cut protein provided the best wet rub resistance of the three NaOH cut proteins tested.

3. NH_4OH cut proteins gave the highest level of wet rub resistance.

RECOMMENDATIONS

AZC provided the lowest viscosity NaOH cut protein coatings, and at high levels of addition, produced wet rub results which approached NH_4OH cut protein coatings. The amount of wet rub resistance was also proportional to the amount of AZC added. Therefore, it should be possible to obtain the wet rub results required with increased levels of addition. AZC at levels (3.5–8) percentage could possibly produce the insolubilization required.

Within the group of insolubilizers tested, glyoxal produced the best wet rub and wet pick results using the NaOH cut proteins. The property hindering its use is the high viscosity. Various fluidizers could be tested to determine if the viscosity could be lowered to a usable range.

Data from Tappi monograph 22 indicates that the percentage NaOH used to cut protein can be reduced at higher cooking temperatures. If this is true, it should be possible to get complete protein dispersion while maintaining a low level of sodium salts in the finished coating.

Temperature, °C.	45	55	65	85
Minimum amount of caustic soda, %	3.0	2.5	2.2	2.0
pH of dispersion at 30°C.	8.3	7.5	6.93	6.5

An alternate solution to the ammonium problem might be to reduce the amount of NH_4OH in the coating system rather than eliminating it completely. This could be done by using combinations of NaOH and NH_4OH to cut the protein. The method described might combine the improved dry pick strength of the NaOH cut proteins and the superior wet rub resistance of the NH_4OH cut protein.

Improvements in Experimental Design

To improve the accuracy of test data the following changes in experimental design should be made:

1. A higher protein level in the finished coating would increase the wet and dry pick values making them more reproducible.

2. A control coating with zero insolubilizer level should be tested to determine if any additives had an adverse effect on the coating properties.

3. The drawdown method used produced a large deviation in coat weights. A more precise method of coating application would improve testing accuracy.

4. The protein, pigments, and insolubilizer were all blended simultaneously. An improved method would be to mix the insolubilizer with the protein before adding the pigments.

5. A time study was originally planned for this project but was abandoned due to problems encountered with the turbidimeter used for the wet rub rating. It would be valuable to know how the coating properties varied with time.

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APPENDIX

COATING COMPONENTS FOR NH_4OH CUT PROTEIN COATINGS

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
A-1	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	ProCote 200	14.2	13.0	91.5
	AZC .75%	20.0	0.15	0.75
	H_2O	0.0	10.0	16.99
	TOTAL	45%	113.15	251.44
A-2	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	AZC 2.0%	20.0	0.4	2.0
	H_2O	0.0	0.0	16.3
	TOTAL	45%	113.4	252.0
A-3	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	AZC 3.5%	40.0	0.7	3.5
	H_2O	0.0	0.0	15.46
	TOTAL	45%	113.7	252.66
A-4	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	Glyoxal 2%	40.0	0.26	0.65
	H_2O	0.0	0.0	17.34
	TOTAL	45%	113.26	251.69
A-5	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	Glyoxal 4%	40.0	0.52	1.3
	H_2O	0.0	0.0	17.3
	TOTAL	45%	113.52	252.3
A-6	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	Glyoxal 6%	40.0	0.78	1.95
	H_2O	0.0	0.0	17.19
	TOTAL	45%	113.78	252.84

COATING COMPONENTS FOR NH_4OH PROTEIN COATINGS

(Cont.)

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
A-7	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	MF `5%	80.0	0.65	0.8125
	H_2O	0.0	0.0	18.04
	TOTAL	45%	113.65	252.55
A-8	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	MF 7%	80.0	0.91	1.137
	H_2O	0.0	0.0	18.3
	TOTAL	45%	113.91	253.13
A-9	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	MF 10%	80.0	1.3	1.625
	H_2O	0.0	0.0	18.675
	TOTAL	45%	114.3	254.0
A-10	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	SunRez 2%	45.0	0.26	0.5778
	H_2O	0.0	0.0	17.4
	TOTAL	45%	113.26	251.67
A-11	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	SunRez 3%	45.0	0.39	0.866
	H_2O	0.0	0.0	17.4
	TOTAL	45%	113.39	251.96
A-12	Clay Hydrafine	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Protein	14.2	13.0	91.5
	SunRez 4%	45.0	0.52	1.15
	H_2O	0.0	0.0	17.4
	TOTAL	45%	113.52	252.25

COATING COMPONENTS FOR 2.5% NaOH CUT PROTEIN COATINGS

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
B-1	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC .75%	20.0	0.15	0.75
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	15.7
	TOTAL	45%	113.475	252.175
B-2	Protein	13.94	13.0	93.21
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC 2%	20.0	0.4	2.0
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	15.0
	TOTAL	45%	113.725	252.7
B-3	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC 3.5%	20.0	0.7	3.5
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	14.02
	TOTAL	45%	114.0	253.41
B-4	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 2%	40.0	0.26	0.65
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	16.02
	TOTAL	45%	113.585	252.695
B-5	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 4%	40.0	0.52	1.3
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	16.0
	TOTAL	45%	113.85	253.025
B-6	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 6%	46.0	0.78	1.95
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	15.7
	TOTAL	45%	114.105	253.68

COATING COMPONENTS FOR 2.5% NaOH CUT PROTEIN COATINGS
(Cont.)

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
B-7	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 5%	80.0	0.65	0.8125
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	16.7
	TOTAL	45%	113.98	253.54
B-8	Protein	13.94	13.0	93.21
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 7%	80.0	0.91	1.14
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	17.0
	TOTAL	45%	114.235	254.165
B-9	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 10%	80.0	1.3	1.625
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	17.3
	TOTAL	45%	114.625	254.95
B-10	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez 2%	45.0	0.26	0.5778
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	16.1
	TOTAL	45%	113.585	252.7
B-11	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez 3%	45.0	0.39	0.866
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	16.1
	TOTAL	45%	113.715	252.991
B-12	Protein	13.94	13.0	93.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez 4%	45.0	0.52	1.15
	NaOH	100.0	0.325	0.325
	H_2O	0.0	0.0	16.1
	TOTAL	45%	113.845	253.27

Note: Actual cut protein % solids = 14.3% total solids.
14.3 total solids x 2.5% NaOH = .3575 of total is NaOH
14.3 total solids - .3575 NaOH solids = 13.94% protein solids

COATING COMPONENTS FOR 3.5% NaOH CUT PROTEIN COATINGS

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
C-1	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC .75%	20.0	0.15	0.75
	NaOH	100.0	0.455	0.45
	H_2O	0.0	0.0	14.86
	TOTAL	45%	113.6	252.46
C-2	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	12.6
	AZC 2%	20.0	0.4	2.0
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	14.19
	TOTAL	45%	113.855	253.04
C-3	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC 3.5%	20.0	0.7	3.5
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	13.4
	TOTAL	45%	114.155	253.755
C-4	Protein	13.8	13.0	94.2
	clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 2%	40.0	0.26	0.65
	NaOH	100.00	0.455	0.455
	H_2O	0.0	0.0	15.22
	TOTAL	45%	113.715	252.725
C-5	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 4%	40.0	0.52	1.3
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	15.2
	TOTAL	45%	133.975	253.355
C-6	Protein	13.8	13.0	74.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 6%	40.0	0.78	1.95
	NaOH	100.00	0.455	0.455
	H_2O	0.0	0.0	14.9
	TOTAL	45%	144.236	253.71

COATING COMPONENTS FOR 3.5% NaOH CUT PROTEIN COATINGS

(Cont.)

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
C-7	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 5%	80.0	0.65	0.8125
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	15.9
	TOTAL	45%	114.11	253.57
C-8	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 7%	80.0	0.91	1.14
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	16.2
	TOTAL	45%	114.36	254.195
C-9	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 10%	80.0	1.3	1.625
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	16.5
	TOTAL	45%	114.755	254.98
C-10	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez 2%	45.0	0.26	0.5778
	NaOH	0.455	0.455	0.455
	H_2O	0.0	0.0	15.3
	TOTAL	45%	113.715	252.733
C-11	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez	45.0	0.39	0.866
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	15.3
	TOTAL	45%	113.845	253.021
C-12	Protein	13.8	13.0	94.2
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez	45.0	0.53	1.15
	NaOH	100.0	0.455	0.455
	H_2O	0.0	0.0	15.3
	TOTAL	45%	113.975	253.305

Note: Actual cut protein % solids = 14.3% total solids.
14.3 total solids x 3.5% NaOH = .5005 of total is NaOH
14.3 total solids .5005 NaOH solids = 13.79 = 13.8% protein solids

COATING COMPONENTS FOR 5% NaOH CUT PROTEIN COATINGS

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
D-1	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC .75%	20.0	0.15	0.75
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	13.6
	TOTAL	45%	113.8	252.9
D-2	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC 2%	20.0	0.4	2.0
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	13.0
	TOTAL	45%	114.05	253.55
D-3	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	AZC 3.5%	20.0	0.7	3.5
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	12.11
	TOTAL	45%	114.35	254.16
D-4	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 2%	40.0	0.26	0.65
	NaOH	100.00	0.65	0.65
	H_2O	0.0	0.0	13.9
	TOTAL	45%	113.91	253.1
D-5	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 4%	40.0	0.52	1.3
	NaOH	100.0	0.65	0.655
	H_2O	0.0	0.0	13.9
	TOTAL	45%	114.17	253.755
D-6	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	Glyoxal 6%	40.0	0.78	1.95
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	13.8
	TOTAL	45%	114.43	254.3

COATING COMPONENTS FOR 5% NaOH CUT PROTEIN COATINGS

(Cont.)

Coating Designation	Material	% Solids	Dry Parts	Wet Parts
C-7	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 5%	80.0	0.65	0.8125
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	14.68
	TOTAL	45%	114.3	254.04
C-8	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 7%	80.0	0.91	1.14
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	14.93
	TOTAL	45%	114.56	254.62
C-9	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	MF 10%	80.0	1.3	1.625
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	15.3
	TOTAL	45%	114.95	255.47
C-10	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez	45.0	0.26	0.578
	NaOH 2%	100.0	0.65	0.65
	H_2O	0.0	0.0	14.0
	TOTAL	45%	113.91	253.128
C-11	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez	45.0	0.39	0.866
	NaOH	100.0	0.65	0.65
	H_2O	0.0	0.0	14.6
	TOTAL	45%	114.04	253.42
C-12	Protein	13.59	13.0	95.7
	Clay	70.0	90.0	128.6
	TiO_2	73.5	10.0	13.6
	SunRez	45.0	0.52	1.15
	NaOH	100.00	o.65	0.65
	H_2O	0.0	0.0	14.1
	TOTAL	45%	114.14	253.8

Note: Actual cut protein % solids = 14.3 total solids
14.3 total solids x 5% NaOH = .715 of total is NaOH
14.3 total solids - .715 NaOH solids = 13.59% Protein Solids