

BUSINESS CONFIDENTIAL

PROJECT REPORT

USE OF ASBESTOS AS A PIGMENT IN PAPER COATINGS

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SUMMARY The constantly rising costs of mailing publications has promoted an intense interest in ways of reducing the weight of paper and paper coatings employed. Currently, the use of needle shaped pigments to lower the density and increase the coverage of paper coatings has been attracting much attention. Since Carbide's high-purity chrysotile asbestos approaches the dimensions of the needle shaped pigments currently being promoted as useful in this application, its use in paper coating formulations was investigated, and found to be feasible.

The asbestos can be dispersed together with typical clay pigments to form reasonably fluid dispersions at up to 25% asbestos based on the clay. At higher concentrations, the viscosity increase is so great that the dispersions must be diluted to impractically low levels (under 45% total solids). No difficulty was experienced in coating the clay-asbestos formulations, but attempts to use 100% asbestos resulted in serious streaking problems which could not be overcome.

The asbestos imparts increased brightness, opacity, and ink holdout to coatings when used in the optimum range of 5 to 10% asbestos in the pigment. Some decrease in pick resistance was noted in this range. Most of the increase in brightness and opacity is lost when the coating is calendered on smooth rawstock, but the loss is minimized on rough rawstock.

Indications are that asbestos will be useful in base coats to fill rough rawstocks efficiently, or on lightweight publication papers. A patent memo has been written concerning the use of asbestos in paper and board coatings. It is planned to discuss these results with paper companies to determine their interest.

INTRODUCTION Within the last year a growing interest in the use of needle-shaped pigments has been noted in the paper coating field, particularly for publication papers. This is exemplified by two papers dealing with such pigments presented at the Coating Conference in May 1969 (1)(2), and much discussion among the personnel present.

RESEARCH AND DEVELOPMENT DEPARTMENT
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The interest in needle shaped pigments arises from the desire to achieve lower bulk densities in the coatings for publication grades of paper. Needle shaped pigments do not pack as densely as the platelet-shaped clay particles currently used as the main pigment in paper coatings. When mixed with clay, the needle shaped pigments tend to lower the bulk density of the mixture without seriously detracting from the smooth surface normally obtained with clay coatings. Examples of needle-shaped pigments currently being investigated are PKT (a potassium titanate), acicular calcium carbonate, and a new analog of Satin White as yet unidentified. Satin White itself which has been virtually obsolete for some years is also being reexamined for possible utility in this special application in spite of the difficulty in handling this material.

The reason behind this sudden interest in needle shaped pigments is the current high cost of mailing and the fear that postal rates will continue to rise. To exercise some control over this major cost item, publishers are demanding a lighter weight publication paper. Currently, the average publication paper has a 36-lb basis weight, based on a 28-lb rawstock coated with 4 lbs of coating on each side. Some 34-lb basis weight paper is being made and the goal is 30 to 32 lbs. Since it is virtually impossible to get a rawstock of less than 25 or 26 lbs with sufficient strength to withstand the coating operation the coat weight must be reduced to 2 or 3 lbs per side, causing a seriously decreased opacity and low ink holdout. Correction of the opacity with titanium dioxide is possible, but the expense seriously detracts from the possible savings. Therefore, means of lowering the density of the coating are being sought. Obviously with a lower density coating, a thicker coating will result at the same coat weight per unit area, and an increase in thickness will usually result in greater opacity.

Previous work by Buttrick (3) and Kelly (4) had indicated that asbestos might have some application in this field. The shape of the Carbide high-purity asbestos fibers approaches that of the needle-shaped pigments currently being investigated. It also has a high brightness and is relatively cheap, both of which are highly desirable in a pigment. Furthermore, asbestos has been shown to be synergistic with titanium dioxide in other applications, which would be advantageous if additional opacity was desired.

For these reasons a further investigation of asbestos in publication papers was initiated. This report discusses the preparation of asbestos-clay dispersions, the effect of asbestos on the coating properties, the effect of calendering on the coating properties with asbestos, and the possible utility of asbestos in several types of coatings.

DISCUSSION Asbestos tends to absorb large amounts of water and to mat together, so that only dilute suspensions flow readily, and these tend to settle out rapidly on standing. From the previous work of Buttrick and Kelly (3)(4) it appeared that the usual clay dispersants would work on a mixture of clay and asbestos to give reasonably fluid dispersions at high solids.

As a first step in this investigation, the amount of asbestos which could be successfully dispersed in clay to give a reasonable viscosity at 70% $\bar{\Sigma}$ was explored with two types of clay - a #2 coating clay (HT clay) and a delaminated clay (Nuclay). The results are shown in Table 1.

The delaminated clay gave lower viscosities than the No. 2 coating clay, by almost exactly half in the 7-1/2% asbestos dispersion, paralleling the difference in the viscosity without asbestos.

It appears that up to about 10% asbestos can be tolerated in the clay dispersion at 70% solids without exceeding a practical viscosity for the handling of the dispersion. At 20% asbestos, the solids of the dispersion must be reduced to about 55% solids for easy handling. At 100% asbestos, a very poor dispersion is obtained with poor flow properties. The total solids had to be reduced to 20.9% to obtain a marginally acceptable flow. Thus, the practical limit of the use of asbestos appears to be about 25% by weight of the clay in a dispersion, as at higher asbestos levels, the total solids of the dispersion must be reduced to such a low level that the formulation of most coating colors becomes difficult or impossible.

Asbestos as a "High Bulking" Pigment

In order to evaluate the bulking properties of asbestos, two of the clay-asbestos slurries (7-1/2% asbestos) were diluted with water and allowed to settle 5 days in graduated cylinders in comparison with plain clay slurries. The dilution was 170 g of slurry (approximately 100 ml) diluted with 200 g of water. The results were 69 ml of settled Nuclay vs 91 ml of the Nuclay-asbestos slurry; and 69 ml of #2 coating clay vs 110 ml of clay-asbestos slurry. There was no evidence of flocculation, as the clay-asbestos sediment was well packed and difficult to redisperse in the supernatant liquid.

The asbestos increased the bulk of the settled clay from 32 to 59.5%, confirming our theory that asbestos should be a high-bulking pigment in combination with clay.

Water Retention

Although asbestos significantly increased the viscosity of the clay slurry, the water retention of the slurry was slightly decreased by asbestos. Using the Baroid filter test for water retention, a 70% clay slurry gave a filtrate of 9.5 ml whereas a 65% clay-5% asbestos slurry gave a filtrate of 11 ml. (In this test, increased water retention is demonstrated by a decreased volume of filtrate when 300 g of slurry is subjected to filtration under 100 psi air pressure for 30 minutes. Excellent water retention would be less than 2 ml filtrate.)

Good water retention in a coating minimizes binder migration, dewatering at the point of application, and helps prevent streaking.

Even in the form of a simple coating color with Dow 620 latex, the clay-asbestos pigment gave 7.0 ml of filtrate as compared with 6.0 ml for the control with no asbestos.

It is evident that the asbestos contributes nothing in the way of water retention to the pigment slurry or to coating colors, and if anything, it is slightly detrimental to water retention.

Effect on Coating Properties

Clay-asbestos pigment mixtures perform well in the laboratory trailing blade coating process at levels up to 20% asbestos in the pigment. However, due to the low total solids of the coating colors at this level, the exploration of higher concentrations was not undertaken, except for one attempt to use asbestos as the sole pigment in a coating color. When 100% asbestos was formulated with 16% oxidized starch, based on pigment, as a binder, it was impossible to coat smoothly with either a trailing blade or a wire-wound rod. The asbestos fibers bunched up in the nip of the blade or rod and produced severe streaks. Variations in pressure on the blade, speed, and several types of substrate (Andover, Time-Life, and unbleached Kraft) made no noticeable difference in the tendency to streak.

It is believed that up to 25% asbestos could be incorporated into a coating color with clay before the high viscosity forced the total solids down to an impractically low level for easy handling and use in most coating processes, but higher levels would be impractical.

Fifteen coating formulations were made up with asbestos contents of from 5 to 20% of the pigment, using starch and starch-latex binder systems and two varieties of clay, a #2 coating clay and delaminated clay. These formulations are shown in Tables II and III. The coatings were applied to a lightweight publication paper (Time-Life) and to heavier weight coating stock at coat weights from 3 to 13 lbs per ream. The properties of the coated paper are given in Tables IV and V.

In examining the properties of the uncalendered coated papers it is apparent that brightness and opacity show consistent improvement of 1 to 2 points with asbestos present as compared to the controls with no asbestos. The ink holdout is also improved by asbestos with high-starch binders, but with the 14-4 latex-starch binder the ink holdout is slightly lower. The porosity and pick resistance are generally decreased by asbestos, but the decreases are not so large as to be a serious problem in most applications.

The brightness and opacity improvement with asbestos should be particularly attractive in lightweight publication papers as pointed out previously; and the high-bulking characteristics should also be particularly useful in base coats on rough substrates.

Effect of Calendering

On supercalendering, the brightness and opacity of all the sheets was lowered as expected. Unexpectedly, however, the advantage in brightness and opacity with 5% asbestos was largely lost on supercalendering (Table IV). This was disappointing and puzzling. A possible explanation was that the asbestos in the coating caused the coating to have an internal porous structure similar to "bubble coating", which was collapsed on

supercalendering. The internal structure would contribute to increased brightness and opacity by multiple refraction at the coating interfaces within the porous coating, and these interfaces would be lost if the coating were compressed or collapsed from the pressure of calendering. If such porosity existed, it would have to be of the unbroken bubble type, as the porosity of the coating by air permeability is decreased by the presence of asbestos except at the higher levels of asbestos in the coating.

It was reasoned that a coating on a rough substrate should lead to less loss in brightness and opacity, as the roughness of the substrate would partially protect the coating from excessive pressure in passing through the calender. That is, the high spots in the substrate would carry a high percentage of the load, leaving the coating in the valleys with less pressure. This was tried by coating a coarse brown Kraft paper with two formulations: H (control) and I (containing 7-1/2% asbestos in the pigment) (Table III). The two coatings were applied simultaneously with a blade coater - one coating on the left half and one on the right half of the blade. The resultant side by side coating showed clearly that the side with asbestos gave better coverage of the brown paper than the control. The difference persisted even after supercalendering at 1000 pli and 150°F, 2 passes. After supercalendering the side with asbestos measured 64 in brightness against 61 for the control. Both sides measured 100% opacity due to the heavy weight of the Kraft substrate, but on examining the coatings by strong transmitted light, the superior opacity of the side containing asbestos was easily evident to the eye.

Since one of the uses visualized for a needle-shaped pigment is the efficient filling of rough surfaces on paper, it would appear that asbestos would be suitable in this application - not only from the better brightness and opacity, but also from the better holdout due to the higher viscosity, and the increased bulk of the clay-asbestos pigment mixtures.

A patent memo has been written, covering the use of asbestos in coatings at concentrations from 1 to 25% based on the pigment.

FUTURE WORK The feasibility of using asbestos in coating formulations has been demonstrated. The possible use of asbestos in coatings will be discussed with paper companies to determine their interest based on our data. Any further work in this area will depend upon the paper companies' response to the properties we have demonstrated in the work to date.

EXPERIMENTAL The following materials were used in this investigation:

<u>Pigments</u>	<u>Description</u>	<u>Supplier</u>
HT clay	#2 coating clay	Englehard Minerals & Chemicals Co.
Nuclay	Delaminated clay	Freeport Kaolin Co.
Asbestos	HP open	Union Carbide Corp.
<u>Rawstocks</u>		
Andover	50 lb coating stock	Copco Paper Co.
Escanaba	35 lb publication grade	Mead Paper Co.
Time-Life	28 lb publication grade	Time, Inc.
<u>Binders</u>		
Stayco M	Oxidized corn starch - low viscosity	A. E. Staley Co.
Penford gum 250	Hydroxyethylated corn starch - medium viscosity	Penick & Ford Co.
Penford gum 280	Hydroxyethylated corn starch - medium viscosity	Penick & Ford Co.
Dow 620	Carboxylated styrene butadiene latex	Dow Chemical Co.
PCX 10	Carboxylated styrene-acrylic latex	Union Carbide Corp.
<u>Misc.</u>		
TSPP	Tetrasodium pyrophosphate - Tech. (dispersant)	Mathieson, Coleman & Bell
Nopco C104	Calcium stearate, 50% dispersion	Nopco Chemical Co.
Parez 707	Melamine formaldehyde	Cyanamid

Preparation of Dispersions

5% Asbestos

Charge: 1425 g	Clay (predispersed)
75 g	Asbestos HP
2.17 g	TSPP
630 g	Water

The dry ingredients were placed in a Sigma Blade Mixer (1/2 gallon size) and mixed for a few minutes. The water was then added gradually over a space of 5 minutes. Mixing was continued for 30 minutes, and then the dispersion was diluted to 70% by the addition of 14 g of water. The dispersion was fluid, measuring 1520 cps on a Brookfield RVF Viscometer at 10 rpm and 570 cps at 100 rpm. The control was made up in the same way using 1500 g of clay, and 0.15 g of TSPP.

7-1/2% Asbestos

A. Charge: 1480 g Clay (predispersed #2 coating clay)
120 g Asbestos HP
590 g Water
1.94 g TSPP

After dispersion, 100 g water was added to dilute the suspension to 70% $\bar{S}$.

B. Charge: 1480 g Delaminated clay (Nuclay)
120 g Asbestos
5.74 g TSPP
590 g Water

Dispersed and diluted as in A, above.

9% Asbestos

Charge: 2145 g #2 Coating clay 70% dispersion
150 g Asbestos HP
90 g Water
4.5 g TSPP

The slurry and water were placed in the Sigma Blade mixer and the asbestos was added slowly and the mixing continued for 30 minutes. The dispersion was diluted to 70% $\bar{S}$ by the addition of 25 g of water.

20% Asbestos

Charge: 1280 g Delaminated clay (Nuclay)
320 g Asbestos HP
7.0 g TSPP
1190 g Water

The clay, TSPP, and asbestos were mixed in the Sigma Blade Mixer and the water added slowly. The mixing was continued for 30 minutes. At this point the mix was far too thick and viscous and it was necessary to dilute it with 123 g of water to bring the solids down to 55% to get a reasonable viscosity that could be handled.

100% Asbestos

Charge: 1000 g Asbestos HP
10 g TSPP

The asbestos was charged to the Sigma Blade Mixer along with the TSPP, and water was added slowly until a workable mass was achieved. This required 2000 g of water. More water was added during the 30 min. mixing time as the mass remained dry. After 30 minutes, it was necessary to dilute the mixture further to reduce the solids to 20.9% to get a marginally fluid dispersion.

Preparation of Coating Colors

The starches were cooked at the indicated % solids by adding the dry starch to the water with good agitation and raising the temperature to 90-95°C after the starch was thoroughly wetted out. The cooking at 90-95°C was continued for 20 minutes with mild agitation, and the starch solution was then cooled to 50°C.

The coating colors were prepared by weighing out the pigment dispersions and slowly adding the natural adhesive with good agitation, followed by the latex if any and finally the lubricant. Any necessary water in the formulation was added with the pigment dispersion. The viscosity of the coating color was measured at room temperature with a Brookfield RVF Viscometer.

Coatings

The coatings were applied to the rawstock by manual trailing blade or wire wound rod, depending upon the coating weight desired (heavier weights were applied by rod). Some very low coat weights were applied with the Time-Life mechanized trailing blade laboratory coater. However this machine is slow to operate and is only used for very low coat weights or somewhat higher weights (up to about 5 lbs per ream) when very uniform coatings are desired. The coatings were drum dried at 200°F for 30 seconds in each case. Coat weights were measured by weighing a piece of drum-dried rawstock, coating the weighed paper and then reweighing after the coating was drum dried. The coat weight was calculated from the increase in weight and the area of the coated sample to give pounds per ream (3300 sq ft).

Evaluation

All evaluation tests were run by the appropriate TAPPI methods with the exception of porosity:

Brightness T-452, M58 - Photovolt instrument

Gloss T-480, TS65 - Gardner instrument

Opacity T-425, M60 - Photovolt instrument

K&N Ink RC 19 Modified - Stain measured by brightness test

IGT Pick T-499 - modified by use of Westvaco arm inking device

The porosity (air permeability) was measured with the Sheffield porosity tester using the method supplied by the manufacturer. This method is much faster than the TAPPI method (Gurley Porosity) and is quite satisfactory for comparison between samples as in this work. The standard deviation is ± 34 ml/min in a sample averaging 200 ml/min.

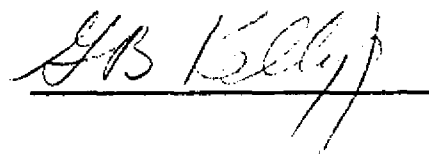
Baroid Filter Test (Water Retention)

300 g of the coating color are placed in the dry Baroid pressure filter on a sheet of Whatman #50 filter paper. The pressure filter is closed and a 25 ml graduate is placed under the outlet. Air at 100 psig is admitted to the filter chamber above the coating color and maintained for 30 minutes. The volume of filtrate is then read. Water retention varies inversely with the volume of filtrate. Coating colors with excellent water retention will show only a slight filtrate (0 to 2 ml) in 30 minutes. Coating colors with very poor water retention show 25-35 ml of filtrate in the same length of time. The Baroid Filter apparatus is obtainable from the Baroid Division of National Lead Co.

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Attachments: 5 Tables

A handwritten signature in cursive script, reading "G.B. Kelly", is written over a horizontal line.

jkg

TABLE I
HP ASBESTOS-CLAY DISPERSIONS IN WATER
USING TSPP AND A SIGMA BLADE MIXER

<u>Clay</u>	<u>% Asbestos</u>	<u>Total Solids</u>	<u>% TSPP (1)</u>	<u>Brookfield Viscosity, cps</u>		<u>Water Retention</u>
				<u>10 rpm</u>	<u>100 rpm</u>	
#2 Coating clay (Predispersed)	0	70	0.30	740	250	9.5 ml, 30 min.
	5	70	0.43	1,520	570	11 ml, 30 min.
	7½	70		1,950	--	--
	9	70	0.37	14,000	6390	--
Nuclay (delaminated)	0		0.3	590	--	--
	7½	70	0.36	1,010	--	--
	20	70	0.44	Very pasty-no flow		
	20	55	0.44	12,650	--	
	100	20.9	1.0	50,000	Tends to dewater on standing	

TABLE II
FORMULATIONS FOR COATINGS

Ingredients	Parts by weight						
	A	B	C	D	E	F	G
#2 Coating clay 70% $\frac{1}{2}$ dispersion (HT clay)	286	--	286	--	286	--	286
Starch - Penford Gum 280, 25% solution	144	144	--	--	--	--	--
#2 Coating clay - 65%) HP Asbestos 5%) 70% dispersion	--	286	--	286	--	286	--
Calcium stearate dispersion 50% $\frac{1}{2}$ (Nopco C-104)	4	4	4	4	4	4	4
Dow 620 Latex 50% $\frac{1}{2}$	--	--	32	32	56	56	--
Starch - Stayco "M" 30% solution	--	--	67	67	27	27	134.5
Water	--	--	<u>4</u>	<u>4</u>	<u>23</u>	<u>23</u>	<u>--</u>
Total solids	55	55	60	60	60	60	57
Binder parts per 100 parts of pigment	18	18	18	18	18	18	20

Reference: 22GBK108

TABLE III
FORMULATIONS AT HIGHER ASBESTOS CONTENTS

Ingredients	Parts by weight									
	H	I	J	K	L	M	N	O		
Delaminated clay 70% dispersion (Nucloy)	286	--	--	--	286	--	286	--		
Delaminated clay 92.5) 70% dispersion HP asbestos 7.5)	--	286	--	--	--	--	--	--		
Starch - Stayco "M" 30% solution	133	133	--	--	133	133	53	53		
Calcium stearate (Nopco C104) 50% dispersion	4	4	4	4	4	4	4	4		
#2 Coating clay 90.9) 70% dispersion HP asbestos 9.1)	--	--	--	286	--	--	--	--		
#2 Coating clay 70% dispersion	--	--	286	--	--	--	--	--		
Starch Penford gum 250 25% solution	--	--	80	80	--	--	--	--		
Acrylic latex (PCX 10) 46% §	--	--	26	26	--	--	--	--		
Starch insolubilizer Parex 707	--	--	3.12	3.12	--	--	--	--		
Water	--	--	40.9	40.9	77	--	77	--		
Delaminated clay 80) 55% dispersion HP asbestos 20)	--	--	--	--	--	364	--	364		
Dow latex 620 50% §	--	--	--	--	--	--	48	48		
Total solids	--	--	55	55	48.3	48.3	51.6	51.6		

Reference: 22GBK129
23GBK7&12
21GBK107

TABLE IV
HP ASBESTOS IN COATINGS

Binder, % and Pigment Penford Gum 280 Starch 18 Control 5% Asbestos	Formulation	% Total Solids	Brookfield		Cool Wt. lb/ream (one side)	Uncoated			Supercoated, 500 g/l - 150% Gloss, 75% Opacity, % K & N Ink Test			Porosity (3" disc) K & N Ink Test			IGT Pick #4 Ink, fpm	
			10 rpm	100 rpm		Brightness, %	Gloss, 75%	Opacity, %								
Control	A	55	12,230	2,952	5.7	71.3	8.0	89	51	325	330	86	56	98.3	300	
	B	55	22,200	4,440	6.4	73.1	8.0	90	52	268	418	71.5	87	90.3	352	
Control					8.8	82.0	10	94	55	39.3	670	81	92	17.8	670	
					9.9	82.0	10	95	58.5	24.3	670	81	92	13.7	670	
Control	C	60	12,900	2,340	6.8	74.5	12	90	49	192	330	61	87	51.7	367	
	D		22,400	3,710	7.2	75.0	12	91	50	228	283	73	87	62.0	303	
Control					8.7	82	14	94	54	31.7	646	81	91	9.3	626	
					9.0	82.8	14	95	56	32.5	540	81	92	8.3	357	
Control	E	60	2,000	398	7.2	73.7	13	90	48	125	378	71	88	28.0	442	
	F		3,980	746	6.6	74.0	14	91	47.5	148	352	72	87	32.3	433	
Control					7.6	83	20	93.7	59.5	29.0	555	81	91	6.7	441	
					8.2	83	19	94.3	58.0	29.3	437	81	92	6.7	527	
Control	G	57	18,640	3,060	4.1	78.5	9	90	59	444	670	78	88	288	670	
			36,100	5,280	4.5	80	10	90	61	112	670	78	89	270	670	
Control					12.7	81	11	94	57	176	670	81	93	112	670	
					13.0	81	11	95	59	80	670	80	94	32	670	

TABLE V
HP ASBESTOS IN COATINGS
HIGHER ASBESTOS CONTENTS

Binder, %, Pigments	Formulation	Total Solids, %	Brookfield		Paper	Coat Wt. (one side)	Brightness, %	Gloss, 75°, %	Coating Properties		Porosity, 3" disc	IGT Pick	
			10 rpm	Viscosity, cps 100 rpm					Opacity, %	K&N Ink Test		#4 Ink, fpm	#2 Ink, fpm
Starch - Stayco "M" 20 Control 7½% sbestos	H	50	3,060	737	Time-Life	3.5	68	40	85.3	58	110	425	--
	I	50	6,480	1,300	"	4.1	69	40	86.0	59	108	288	--
Starch - Penford 10 Gum 250) Acrylic Latex 8 (PCX10) Control 9% Asbestos	J	55	43,300	6,950	Andover	6.25	80.3	--	90.8	63.5	21.2	--	240
	K	55	73,600	9,920	"	6.30	82.6	--	94.3	62	28.6	--	260
Starch (Stayco "M") 20 Control 20% Asbestos	L	48.3	870	282	Time-Life	4.0	71.9	6.6	88.6	45	218	--	500
	M	48.3	5,240	1,192	"	3.6	73	6.4	89.2	43	189	--	670
	L	48.3	870	282	Andover	3.4	83.7	9.5	93.1	60.5	29.2	--	670
	M	48.3	5,240	1,192	"	3.4	84.0	6.5	93.5	52.0	40	--	670
Starch - Stayco "M" 8 Dow Latex 620 12 Control 20% Asbestos	N	51.6	390	109	Time-Life	4.0	72.5	8.8	89.2	46	77	--	315
	O	51.6	8,520	1,256	"	3.3	74	6.2	90.0	41	218	--	455
Control 20% Asbestos	N	51.6	390	109	Andover	3.7	84.2	14.2	93.7	61.5	24.6	--	670
	O	51.6	8,520	1,256	"	3.5	85.0	7.5	93.7	51.5	42.3	--	670
Starch Stayco "M" 20 100% Asbestos	--	20	6,500	1,850	--								

Could not be coated - Streaked badly due to asbestos bunching up in nip of blade or rod.

113A28

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