



4-1996

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Thermo-Chemical Conversion of Starches Using Ammonium Persulfate

By

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**A Thesis
Submitted to The
Faculty of The Undergraduate College
in partial fulfillment for the
Bachelor of Science Degree
Department of Paper Science and Engineering**

Western Michigan University

Kalamazoo, Michigan

April 1996

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Abstract:

The objective of this study was to determine the feasibility of thermal-chemical conversion of corn starch for use in pigmented paper coatings.

Thermal-chemical conversion of starch is capable of creating a wide range of starch solids and characteristics at one location with on-site conversion. It involves the use of high temperatures and pressures, along with a conversion agent (i.e. ammonium persulfate [A.P.], or a peroxide), to hydrolyze and oxidize the unmodified starches.

In this study corn starch was converted using a National Starch Company C-1 Laboratory Jet Cooker. The study was done in three phases. Preliminary work was done to become familiar with the jet cooker operation. Next, three runs were made to prepare starches of different viscosities. These starches were used to prepare coatings which were applied on the CLC coater. Finally, the coated sheets were tested for brightness, smoothness, gloss, and wax pick.

During the running of the jet cooker a number of difficulties were experienced. These included: poor retention, significant dilution due to flashing and quench water, plugging of the retention coil, poor back pressure control and unpredictable starch viscosities.

Runnability during coating of starch as a binder was excellent. The low dewatering effect that starch added to the coating aided in blade coating operability.

The results of the testing of the coatings showed that brightness, smoothness and gloss were best at the medium addition level of A.P. (1.3%). The values of wax pick were indistinguishable from one another because they were within one standard deviation.

These low molecular weights are most often caused by over conversion of the starch structure. The high-shear rheology of the three coating colors was thixotropic, of increasing hysteresis area as binder A.P. level increased. This suggests that as the A.P. level was increased greater reduction of starch molecular weight occurred.

Introduction:

This study involves the thermal-chemical conversion of starches using ammonium persulfate. This method has been criticized over the past several years to the poor resistance of the starches to set back and viscosity instability. The goal of this study is to increase understanding in the conversion process as applied to preparing starches for coating.

The paper industry has been the largest user of starch products for many years. Starch can be modified on-site or pre-modified by an outside supplier. The benefits of on-site conversion include monetary savings and the ability to use one starch source to make several different products for use in the mill.

Thermal-chemical conversion of starch is commonly used for on-site conversion because it can be used to attain starch solids levels for sizing, retention aid, and coating binder type starch applications. It involves the use of high temperatures and pressures, along with a conversion agent (i.e. ammonium persulfate, or a peroxide), to convert the unmodified starches.

In this experiment corn starch was converted in a Laboratory Jet Cooker. The starch was converted to three viscosity levels and used to prepare pigmented coatings. These coatings were applied by a CLC coater and studied for rheological properties. The coated papers were evaluated to relate degree of A.P. conversion to coating properties.

Analysis of Literature:

The paper industry is the largest user of industrial starch. At least 85% of the more than 2 billion pounds of starch used annually by the paper industry is applied at the size press and calender, or used as coating binders. It is estimated that over 90% of this starch is corn- derived (2). Other sources of starches include potato, wheat, tapioca, rice. Each of these starches have inherent properties which affect characteristics of the product. Corn starch has exceptional strength and optical properties at a reasonable price. Of the corn starch used in the industry 30% is unmodified while the remaining 70% is typically modified by the starch supplier (14). The trend of the industry is towards on-site mill conversion of starch.

Starch Fractions

Starch is found as a major carbohydrate product in all plants containing chlorophyll. Chemically is a polymer of glucose. The empirical chemical formula of starch is $(C_6 H_{10} O_5)$. Natural starches have two different types of polymers:

Amylose: A linear straight chained polymer with a molecular weight ranging from 150,000 to 600,000.

Amylopectin: A branched polymer with a molecular weight of 1 to 6 million.

The molecular weight and ratio of amylose to amylopectin depend on the source and of the starch (11). The starch is extracted from the plant in the form of granules.

Starch Modifications

Unmodified starches have undesirable properties and molecular configuration. The definition of an unmodified (native) starch is “that which is obtained by a process which causes the least modification or degradation of the product.” (14) Native starches are generally too viscous at high coating solids content for coating and size press processes. To make these starches more applicable for the paper industry some form of modification to the starch structure is required.

Modified starches have characteristics which make them more suitable for use in the paper industry. The starch is usually lowered in molecular weight via thermal shearing, acid or ammonium persulfate hydrolysis, or enzyme conversion. Starch is degraded ultimately to reduce the viscosity and make it applicable for various stages in the papermaking operation (7). By reducing the viscosity of the starch it allows the starch to be used at higher concentration levels thus improving the filming and adhesive properties (11).

Starches are also termed as premodified. In this process an outside supplier pre-treats the starch adding chemicals such as hypochlorite or ethylene oxide to create derivatives. The starches are washed and redried for transportation to the mills. This method of starch cooking is more expensive to the mills but also provides improved viscosity and solution stability characteristics in the starch dispersions.

Advantages of Unmodified Starch

As with many issues in today's industry the deciding factors are monetary. If modification of starch can be accomplished on a mill basis without going to an outside supplier a key benefit would be the modification of a single base supply of starch which would apply to many functions in the papermaking operation. These applications could include retention aids, surface sizing and coating binders. Savings from on-site modification could be used to justify installation of bulk handling systems that would not be possible had the operation been split between two or more starch products (2). Proponents of on-site conversion claim there is better control and easier adjustment of the starch slurry characteristics to fit changing paper grades and mill applications (2).

Advantages of Premodified Starches

On-site modification has problems such as attendant control and technical and maintenance difficulties which could have been left in the hands of a starch supplier (2). Some general problems include: starch discoloration, inactivation of converted starch slurry, loss of brightness, retrogradation and related storage conditions (2). On-site modification processes also involve the production of water-soluble sugars and low molecular weights that have poor film-forming and binding strength properties (2). Premodified starch suppliers send their starches through a washing process following cooking. This process removes carbohydrate and other chemical by-products which are produced in an on-site conversion system (2). During a PIMA round table meeting concerning starch trends, has several supporters of on-site starches had disheartening information. Mark Johnson, national sales manager, AVEBE America Inc., stated:

“Corn starches have relatively high levels of fats, oils and protein. These materials react with starch during and after cooking, forming highly insoluble sludge. This material can interfere with starch application, viscosity control and severely affect the end quality. The superior filming of high purity starches provides higher and more stable surface strength tests, better printability, and elimination of potential problems such as surface picking, dusting and pigment milking.”

Yet in light of all this turmoil there is still hope. The development of reliable more accurate conversion equipment has eliminated many of the headaches mentioned above. Of course the on-site conversion does offer some complexity concerning commitment of mill resources, compared to the simplicity and invariability of cooking premodified starches. The real commitment depends upon the mill.

Considerations for Starch Selection

The selection of a proper conversion method can be quite difficult. Each conversion process has its strong points and its flaws. There does not exist a pre-set code for determining the proper conversion method, however, some basic guidelines have been established to aid in the struggle.

Attainment of results: The process should provide starch with characteristics which attain the desired paper properties, machine speeds, effluent loads, etc.

Handling of starch: The values of convenience, cost factors, and mill capabilities related to transfer, preparation, and storage of the dry and cooked starch may be limiting and decisive points.

Capital investment: The choice between the cost of the starch system and the return on that investment vs. the long-term purchase of premium-priced starch could have both short and long-term effects on the mill profitability.

Technical involvement: Mills reluctant to commit on a continuing basis the time, training, and expenses needed for the proper operation, adjustment, and maintenance of a starch modification system should choose the relative simplicity of merely cooking a premodified starch.

Personal preference: The likes, dislikes, and experience of individual mill personnel are important, but are hard to quantify (2).

Thermo-chemical Conversion Advantages

There are many conversion processes to choose from including: enzyme, acetylation, oxidation, etherification, thermal, and thermo-chemical. Of these one seems to predominate. Grain Processing Corporation found in their studies that the thermo-chemical conversion process was best suited for their criterion. The conclusion were based on the following premises:

- a.) the process utilized a base starch product available from numerous sources
- b.) predictable viscosity levels could be obtained by varying the oxidant level while holding the temperature and retention time constant
- c.) relatively short retention time were required to provide process changes with minimal waste (3).

The study also offered some insight as to the best oxidant. It was found that because of its lower cost, ease of handling, and the fact that no catalyst was needed to ensure

complete reaction under normal operating conditions, ammonium persulfate was the most suitable oxidation agent (3). Richard Harvey found these benefits to thermo-chemical conversion technology:

- a.) one system could be used for all starch preparation in the mill from low solids content for wet-end application to intermediate solids for sizing to high solids for coatings
- b.) unmodified starch could be used for both high and low solids starch slurries, thus reducing cost and simplifying inventory
- c.) changes from one application to another could be made easily and rapidly
- d.) starch amount was easily regulated
- e.) uniformity of starch and coating was greatly improved because slurries were less sensitive to variations in starch quality (5).

Variables of Thermo-chemical Conversion

Insight into the advantages of the thermo-chemical conversion of starches using ammonium persulfate has led to its operation and implementation. The general form of thermo-conversion utilizes high temperature and pressure to convert a premodified starch. The addition of ammonium persulfate now makes this apparatus quite sufficient to convert unmodified starches completely. The thermal cooker used for such a conversion is shown in Figure 1. The process utilizes a positive displacement pump and a mixing jet. High pressure and high temperature steam is introduced into the process. The steam elevates the temperature and creates shear in the venturi mixing zone. The holding coil maintains the starch at high temperature and pressure for a 5-7 minute retention time. Ammonium

persulfate is added to the starch slurry prior to injection in to the heating zone to aid in the oxidative hydrolysis of the unconverted starch. The amount of ammonium persulfate utilized, the length of time in the retention coil, and the temperature of the holding coil are all variables which are controlled (14). Typical additions of ammonium persulfate are 0.05 to 0.2% based on starch solids at the temperatures range from 304 to 315 degrees Farenheit (2).

Starch as Coating Binders

Starches are commonly used as binders for coating applications. Besides acting as a binder the starch must act as a carrier for the pigment, impart desirable flow characteristics to the coating color for proper application and leveling, regulate degree of water retention of the coating color, and produce the desired strength, ink receptivity, and ink holdout for optimum printing characteristics (13). In addition to imparting good runnability and printability starch must be easy to prepare, have high adhesive strength, be inexpensive, have a stable viscosity during storage, and be unaffected by external conditions, such as wetting, after being dried (13). Each type of starch has its advantages and disadvantages. In many instances the choice of the most satisfying binder becomes a question of rheology. The thermo-chemical conversion process has been highly scrutinized for several years now. The reason for scrutiny can not go unjustified. This process offers many instabilities without adequate control. Temperature exceeding the recommended 315 degrees Farenheit can result in scorched starch, thus affecting the sheets finished brightness. Insufficient retention time and temperature results in incomplete starch modification. The control of pH is imperative in the process for both

conversion and retrogradation control. Retrogradation is a major concern for starch.

Retrogradation involves the tendency of the starch viscosity to increase upon cooling.

When this occurs the straight-line amylose polymers may begin to line up parallel to each other and precipitate (crystallize) from the solution (14).

Experimental Design:

This study was performed in four major sections: the preliminary work, making of starch slurries, CLC coating runs with varying degrees of ammonium persulfate, and the final testing of the coated sheets.

In the preliminary portion of this experiment extensive work was done with the C-1 laboratory provided by National Starch Company. The C-1 cooker is a thermal jet cooking system capable of high temperature and solids. A schematic of this apparatus is shown in Fig. 1 of this paper. The starch and ammonium persulfate slurry is passed through the jet cooker via a positive displacement pump. The starch contacts high temperature steam as it passes through the jet. Once through the cooking jet the starch is held in a holding coil for approximately 3.25 minutes. The suggested holding time is 5-7 minutes, however, this was not possible. The volume of the retention coil was 0.225 gallons and the lowest rating of the positive displacement pump was 0.1 gpm. This would suggest a hold time of only 2.25 minutes. However, slightly longer times were observed. Starch is held in the holding coil for the desired time by using a manual back-pressure regulator. The starch slurry then flashes to the flash chamber and exits in its converted form.

The preliminary work involving the thermal cooker involved setting preliminary starch runs to understand the reaction of the corn starch and the limitations of the jet cooker. First the jet cooker was run with 15% solids and a high degree of ammonium persulfate, approximately 1.0% based on starch solids. The solids were increased slightly while keeping the persulfate level constant. The goal was to achieve 25% outgoing starch

solids. This was quite difficult considering the quench water and stem flash tended to add 30% moisture to the system. The next attempt was to back the level of ammonium persulfate out of the system while keeping the starch solids entering at a constant level. The Brookfield viscometer was used to measure the viscosity of the outgoing solids at approximately 170 degrees. Some typical Brookfield viscometer plots of coating color solids from another experiment are shown in Figs.2&3. This figure shows that typical ammonium persulfate levels are in the 0.15-0.35% range based on starch solids. These persulfate levels were impossible to achieve given the operating difficulties encountered in the jet cooking apparatus which will be discussed later in this paper. From these Brookfield viscometer plots three ammonium persulfate level ranges were targeted on a 32% in-going starch slurry. The levels included the addition of 1.0, 1.3 and 1.5% ammonium persulfate based on starch solids and were titled high, medium and low viscosity, respectively. It was however found that the viscosities did not deviate from one another. The ranges were all reasonably close to 50 Centerpoise at 100 rpm.

In the second phase of the experiment the starches having three viscosities mentioned above were remade and put into coating colors for trial on the CLC coater. It was found that the maximum achievable coating solids with the given starch binder solids was only 55.3%. The formulation and addition levels for one of the coating solids is shown in Table 3.

The values were all calculated and then multiplied 20 times to give the desired amount of coating for the CLC coater. The coating colors were blended and adjusted to a pH of 7.2 to 7.5 using a 10% solution of NaOH. The NaOH significantly decreased the viscosity of

the final coating color. The starch binders were found to have very low pH so a significant amount of NaOH was require (between 8 and 10 droppers). The coating colors were then tested for Brookfield and Hi-Shear viscosity. The coatings were then applied on the CLC laboratory coater. The CLC was run at 2000 fpm with a 20 second pre-dry at 50% power and a 40 second post-dry at 100% power. The delay distance was 3 meters. Each different ammonium persulfate level starch coatings were run with the coat weight targets of 17, 12 and 7 grams per square meter. With these values it was possible to interpolate the results of experimentation to a medium coat weight and relate the different binders accordingly. The coatings ran fairly smoothly and the maximum amount of trials to achieve the three coat weights was 6 with the 1.3% A.P. based on starch as seen in Table (1). The sheets were then put into the humidity lab for two days to condition.

The third phase of the experiment involved the testing of the coated grades. The coated sheets were tested for calendered and uncalendered gloss, smoothness, brightness and wax pick. The procedures for these tests were as prescribed in the TAPPI Test Methods. The results were then analyzed and comparisons were made. Evaluations of these sheets will be discussed in the following results and discussion portion.

Results:

The following coating property results were interpolated to a coat weight of 11.96 g/m² using the three target coat weight values for each of the starch binder make-ups.

The results of Fig. 7 are those for the effects of ammonium persulfate level on the Brookfield viscosity of the coating colors. It is noticed that as the level of ammonium persulfate in the starch binder increased, then the viscosity of the coating color increased, the opposite of what was expected (more A.P. should give more hydrolysis and lower viscosity). The pH's of the 1.5, 1.3 and 1.0% A.P. starches were 2.1, 2.3, and 2.5 respectively. In this case it must also be stated that the most NaOH required to increase the pH to the desired 7.2 to 7.5 range was the 1.5% A.P. with 10 droppers, followed by 1.3% with 8.5 droppers, and finally 1.0% with 8 droppers. These viscosity results are quite the opposite of what are expected and will be confronted in greater detail in the discussion section.

The results for the brightness values of the uncalendered and calendered sheets are shown in Figs. 8 and 9. It was found in the uncalendered sheet that the 1.0% A.P. addition level favored the highest brightness, followed by the 1.3% and 1.5% A.P. levels. The brightness value for the 1.0, 1.3 and 1.5% A.P. addition levels were 82.3, 81.7 and 81.6% respectively. The differences are minimal but was important to note. The values for the calendered sheet was quite different. The values of brightness decreased which was expected, but now the highest brightness value belongs to the 1.3 followed by 1.0 and 1.5% A.P. addition levels. These values were 80.5, 80.4 and 80.2 respectively.

Figs. 10 and 11 represent the uncalendered and calendered smoothness values.

From these results it was found that the 1.3% addition level gave the best uncalendered and calendered smoothness values. The uncalendered smoothness value of 1.3% A.P. was 5.81 microns, followed by 1.0% A.P. with 6.39 microns, and finally 1.5% with 6.4 microns. The results for the calendered smoothness followed the same trend. The values of 1.3, 1.0, and 1.5% A.P. levels were 1.98, 2.12, and 2.24 microns, respectively. These results are as expected according to the order from uncalendered with respect to calendered. However, the order in which the values are arranged (i.e. 1.3% being the highest) are in question and will be discussed later.

Figs. 12 and 13 represent the graphs for uncalendered and calendered gloss. These values follow quite closely to the smoothness value, which was expected. For this case, again, 1.3% A.P. level has the highest uncalendered and calendered gloss. The uncalendered gloss values for the 1.3%A.P. was 13.3%, followed by 1.5%A.P. with 12.5%, finally 1.0% A.P. with 12.3%. This is a slight deviation in comparison with the smoothness graph but is not considerable due to the closeness of the gloss values for the 1.0 and 1.5% A.P. levels. The calendered gloss for 1.3, 1.0, and 1.5% A.P. were 49, 44.7, and 44.1% respectively. These values were expected and we go into greater detail in the discussion portion of the paper.

Figs. 14 and 15 are the graphs for uncalendered and calendered wax pick. For the uncalendered sheet the highest wax pick belonged to the 1.5% A.P. level with 7.8, followed by 1.0% A.P. with 7.4 and then the 1.3% addition level with 7. The results for the calendered sheet followed the same trends. The 1.5% A.P. was highest with 7,

followed by 1.0% at 6.8, and finally the 1.3% level with 6.4. These values are all within one standard deviation from one another and, therefore, no significant difference exists between them.

Figs. 4,5 and 6 represent the high shear viscosity measurements for the three coating colors. It can be seen that the graphs all coatings gave a thixotropic flow behavior. Starch which has been properly dissolved is inherently thixotropic and will impart beneficial blade runnability (6). The 1.0% A.P. addition has a maximum torque of approximately 1800 kilodyne per centimeter, with a hysteresis area 419110 RPM/kilodyne/centimeter. Hysteresis is the area between the up and down sloping characteristic of the rheogram. It indicates the amount of viscosity destructive forces apparent in the presence of high shear rates (12). The 1.3% A.P. level exhibited a higher torque near 2000 kilodyne/cm. and a hysteresis area of 626826 RPM/kilodyne/cm. Finally the 1.5% level had the highest torque with almost 2200 kilodyne/cm and a hysteresis area of 924676 RPM/kilodyne/cm.

Figure 1

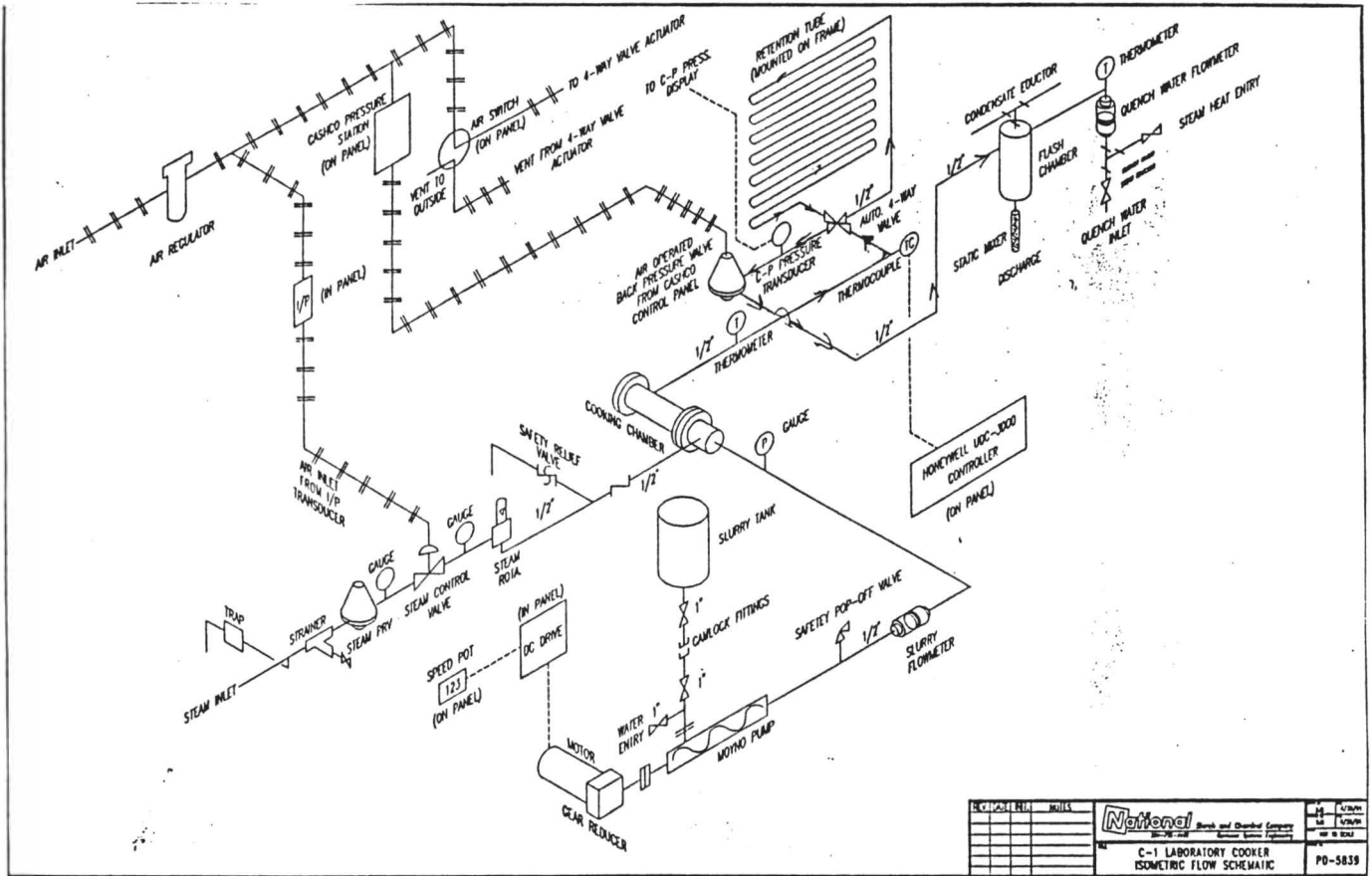


Figure 1 is a schematic of the Thermal Chemical Converter used in this thesis

Figure 2

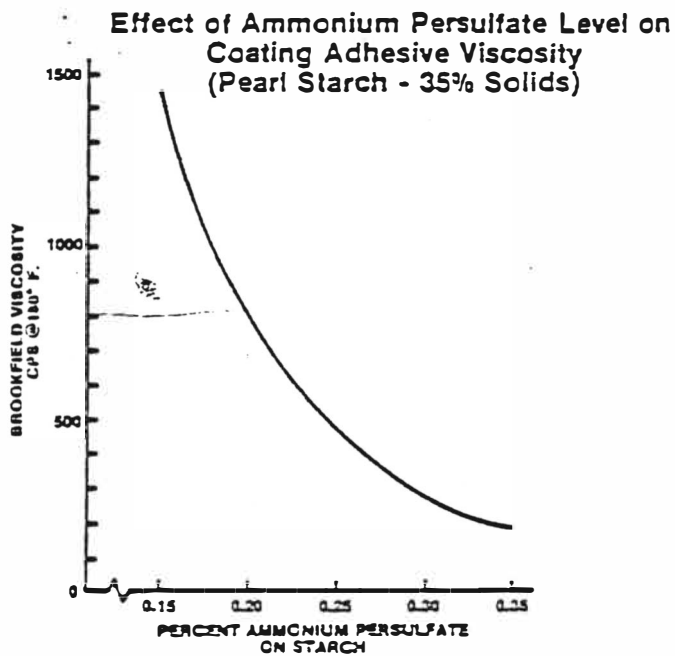


Figure 2 represents the effect of ammonium persulfate level on coating adhesive viscosity

Figure 3

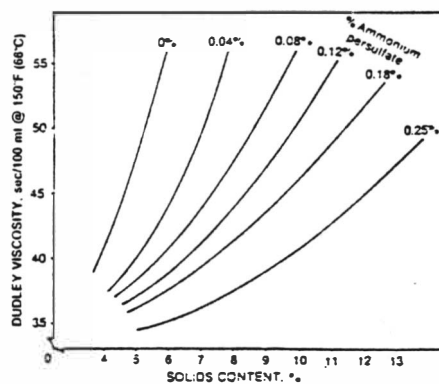


Figure 3 represents typical viscosity curves with increasing amounts of A.P.

Figure 4

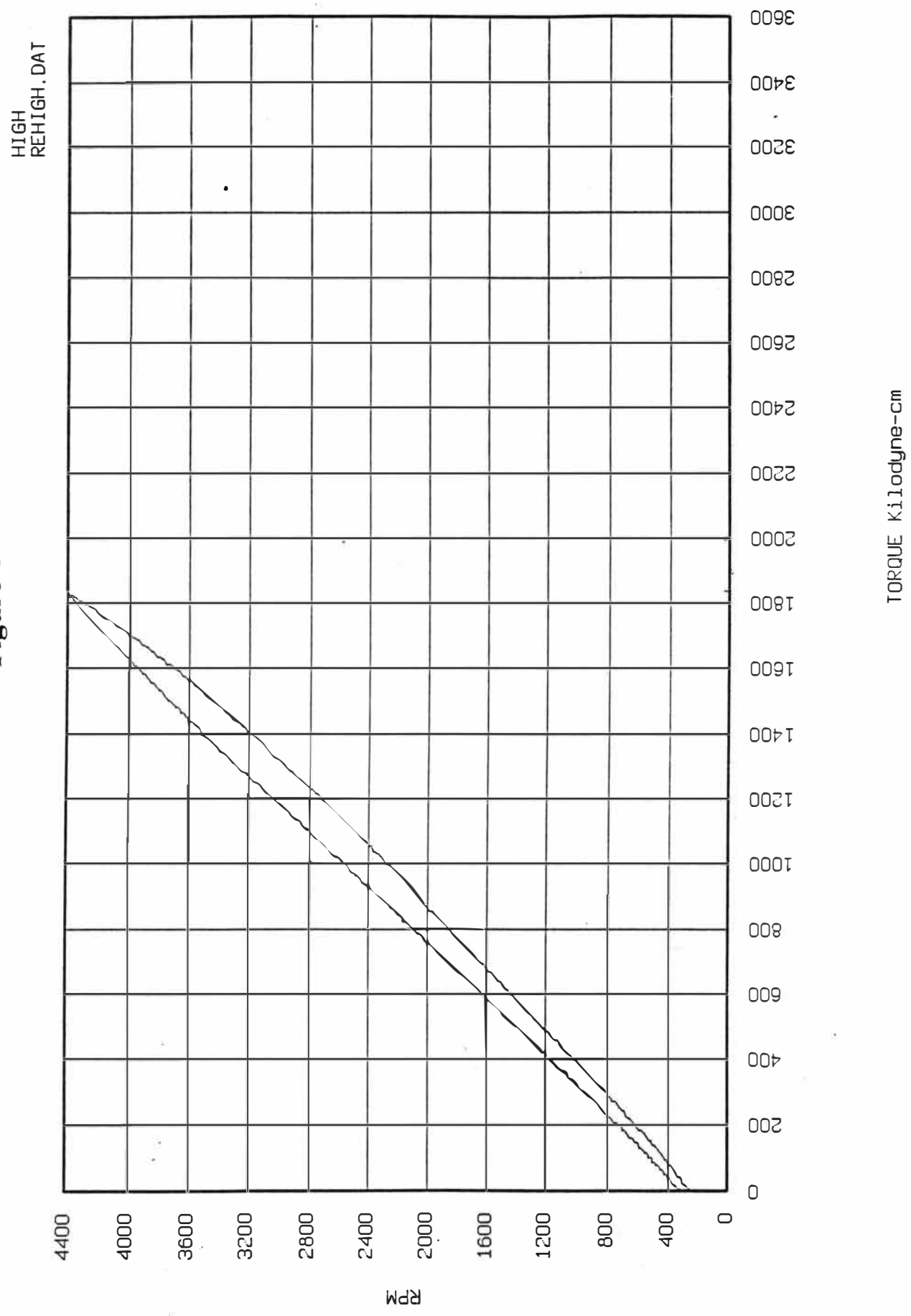


Figure 5

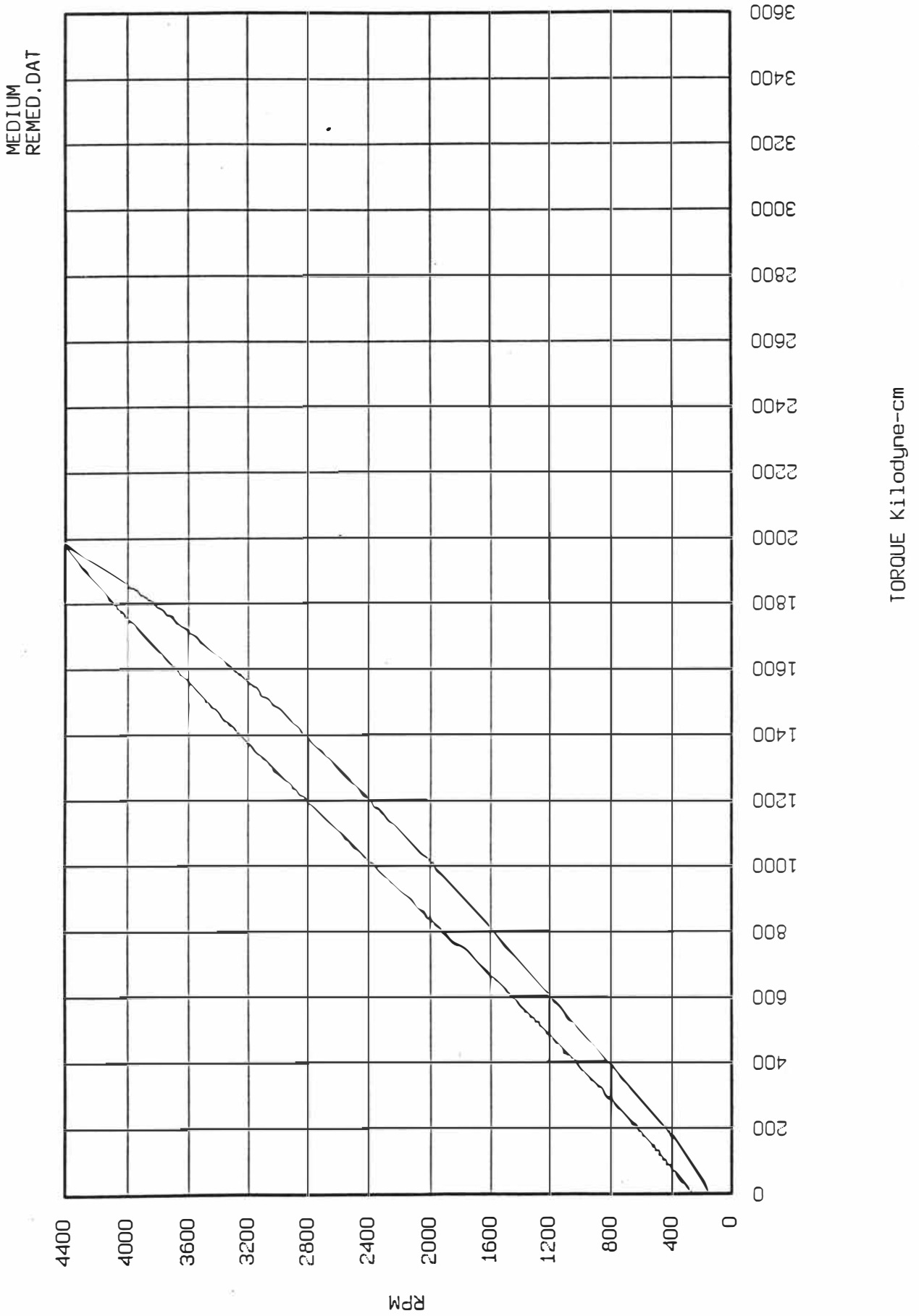
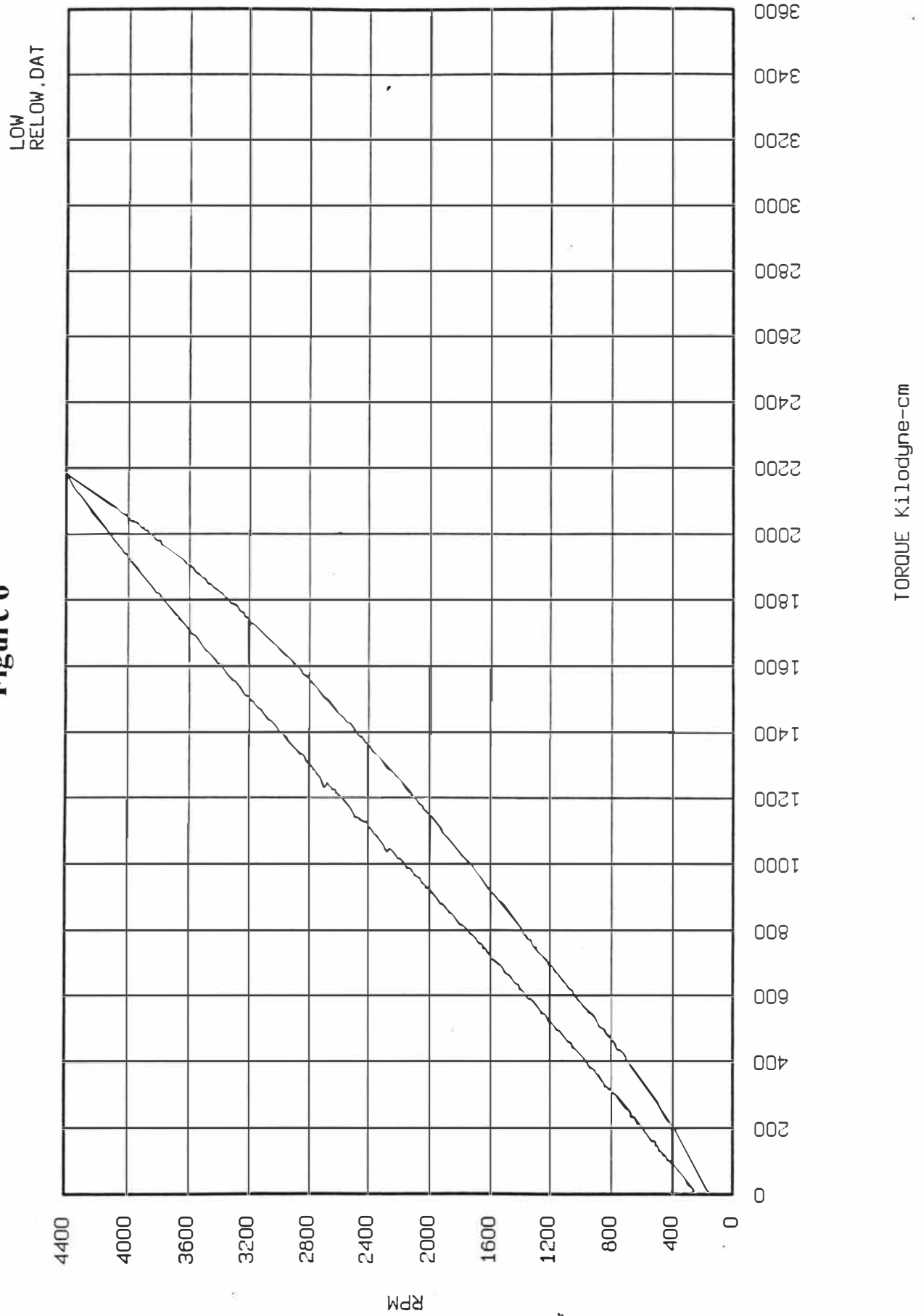


Figure 6



TORQUE Kilodyne-cm

RPM

Figure 7

Viscosity of Coating Colors

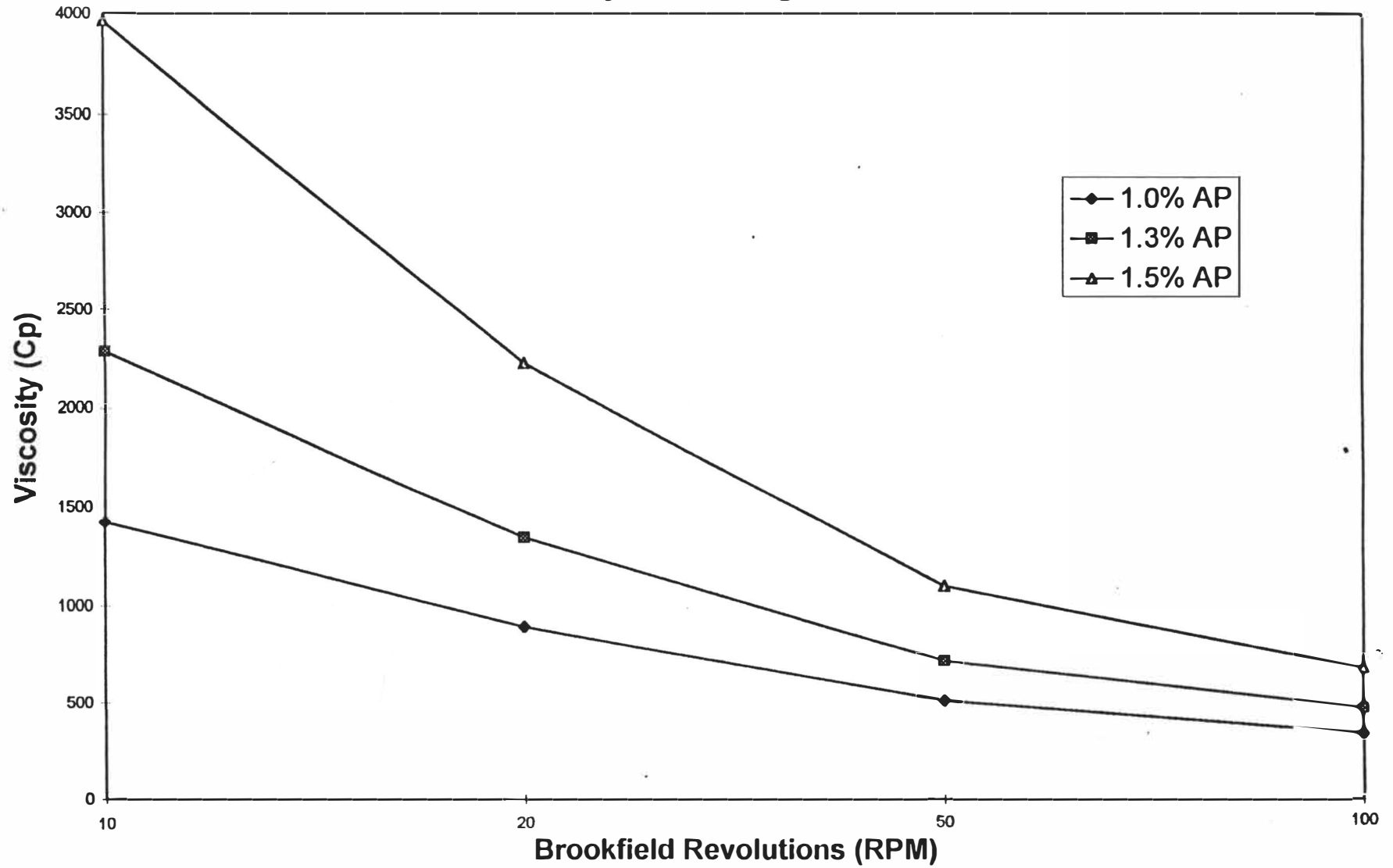


Figure 8

Uncalendered Brightness (11.96 g/m² coat weight)

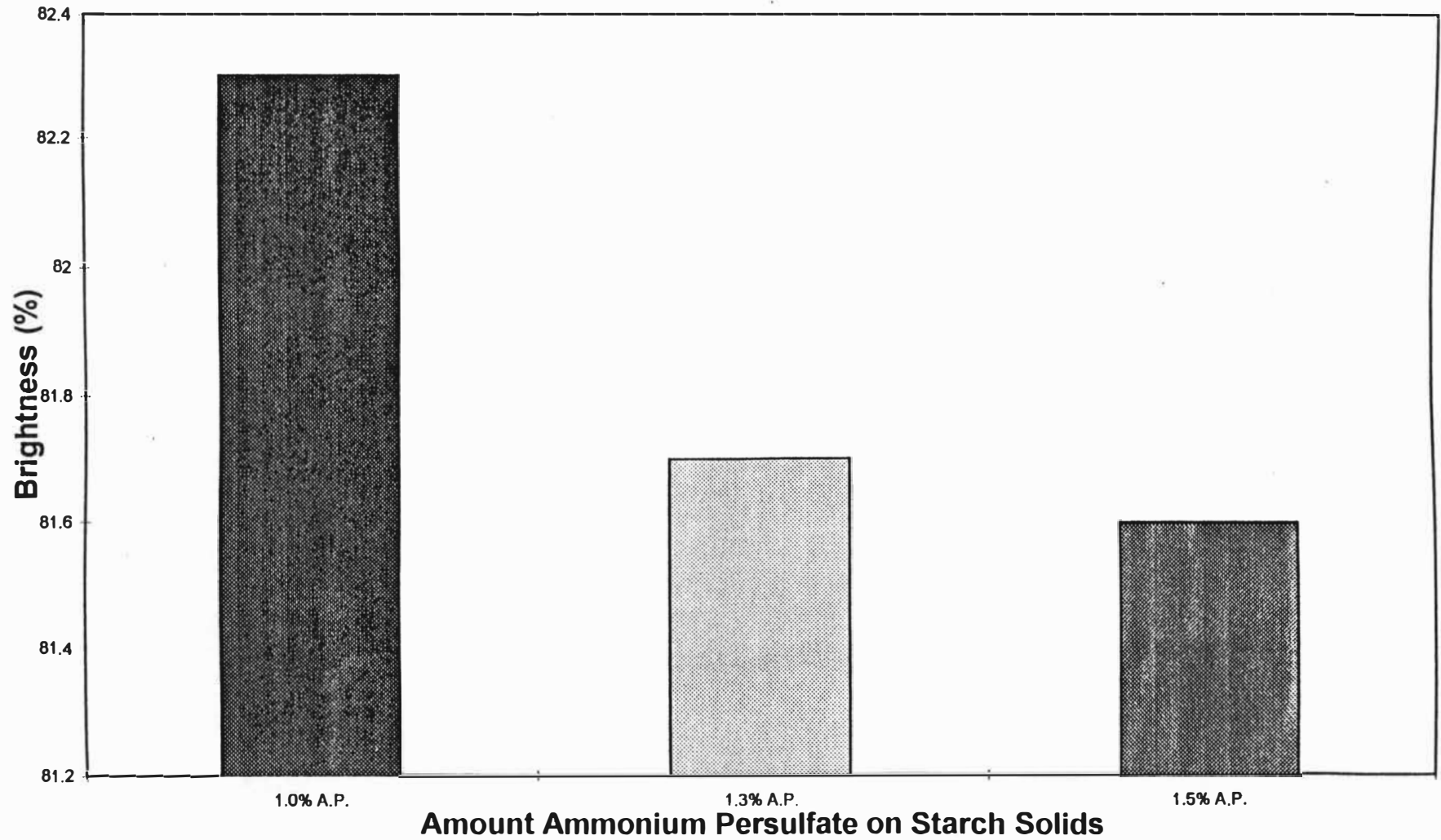


Figure 9

Calendered Brightness (11.96 g/m² coat weight)

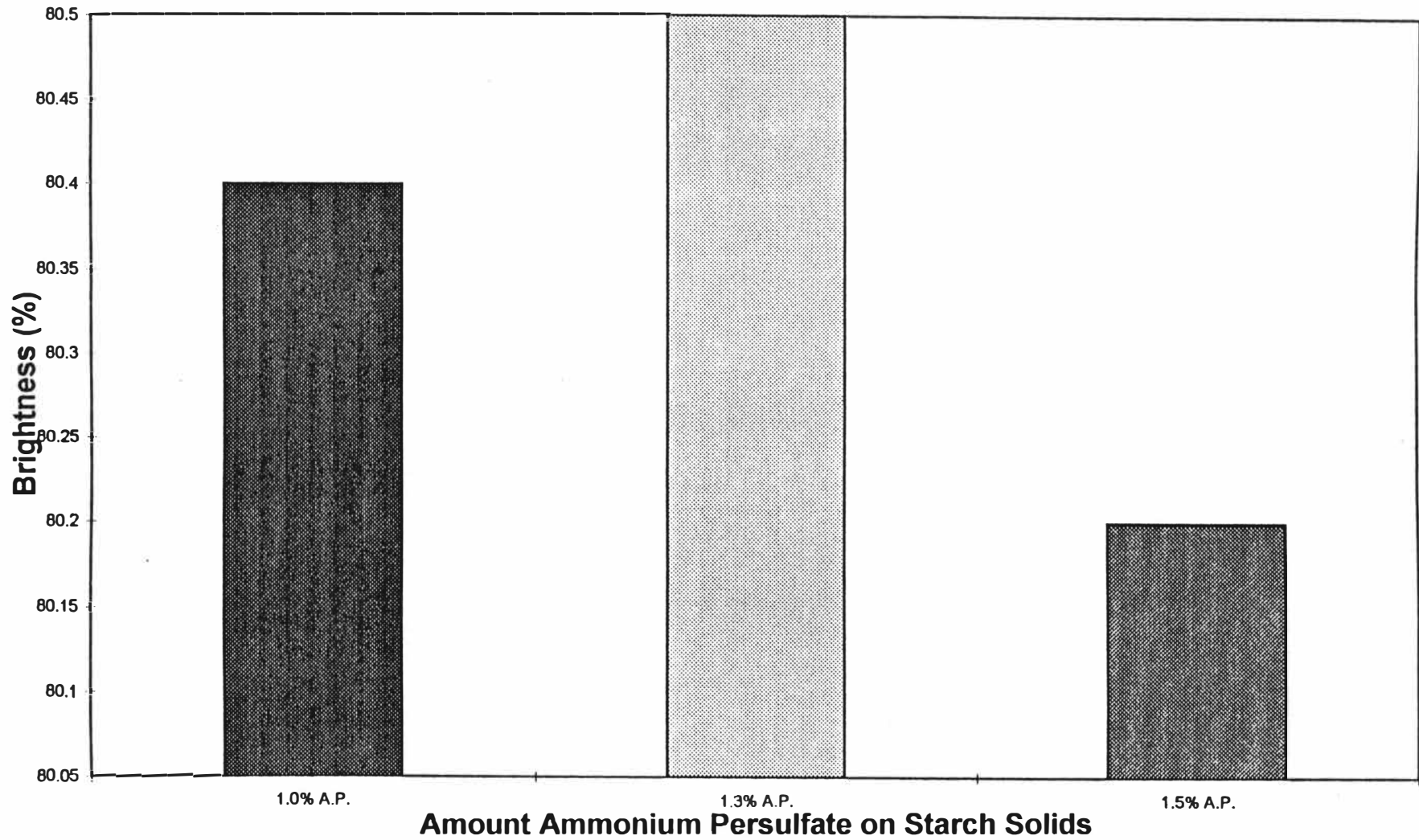


Figure 10

Uncalendered Smoothness (11.96 g/m² coat weight)

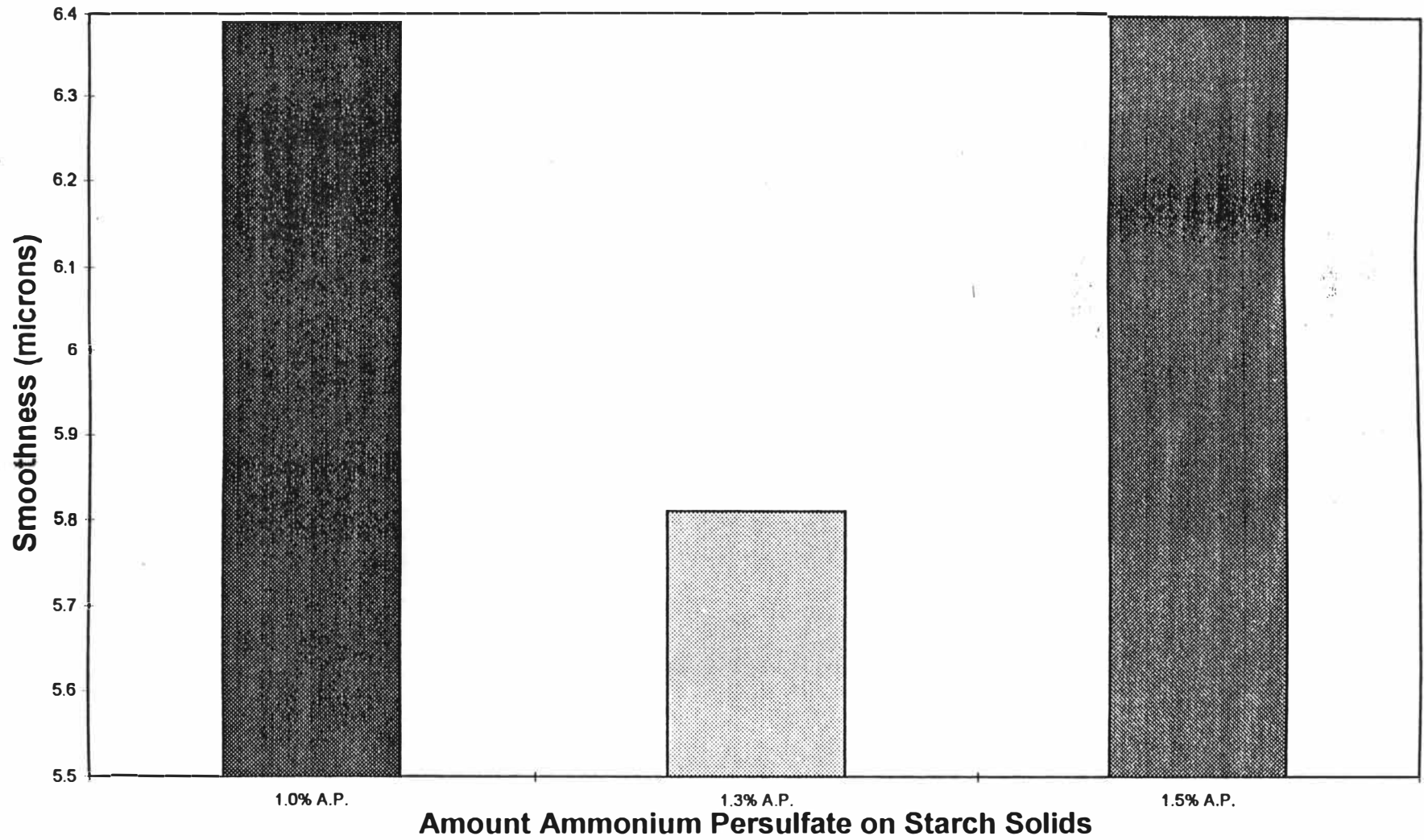


Figure 11

Calendered Smoothness (11.96 g/m² coat weight)

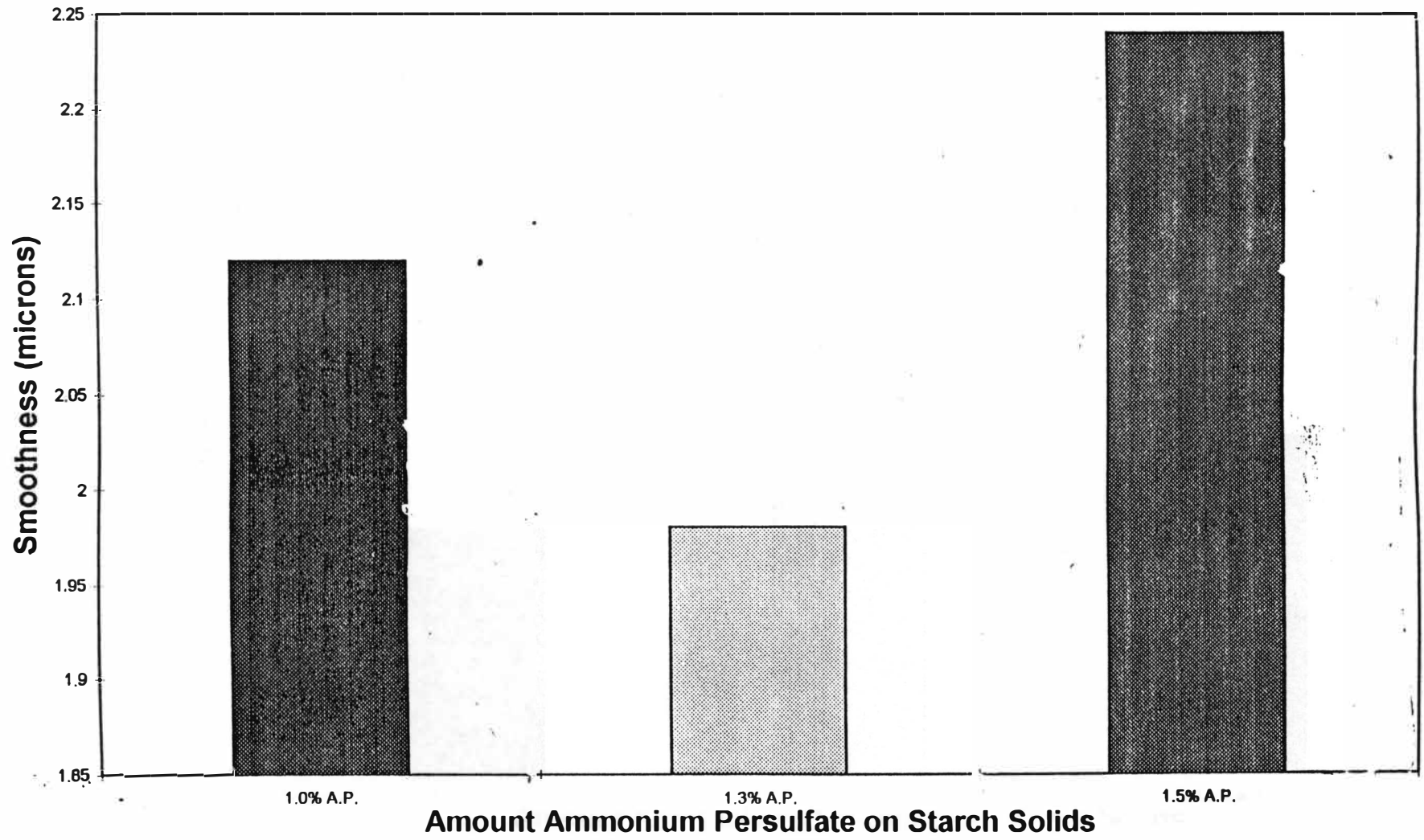


Figure 12

Uncalendered Gloss (11.96 g/m² coat weight)

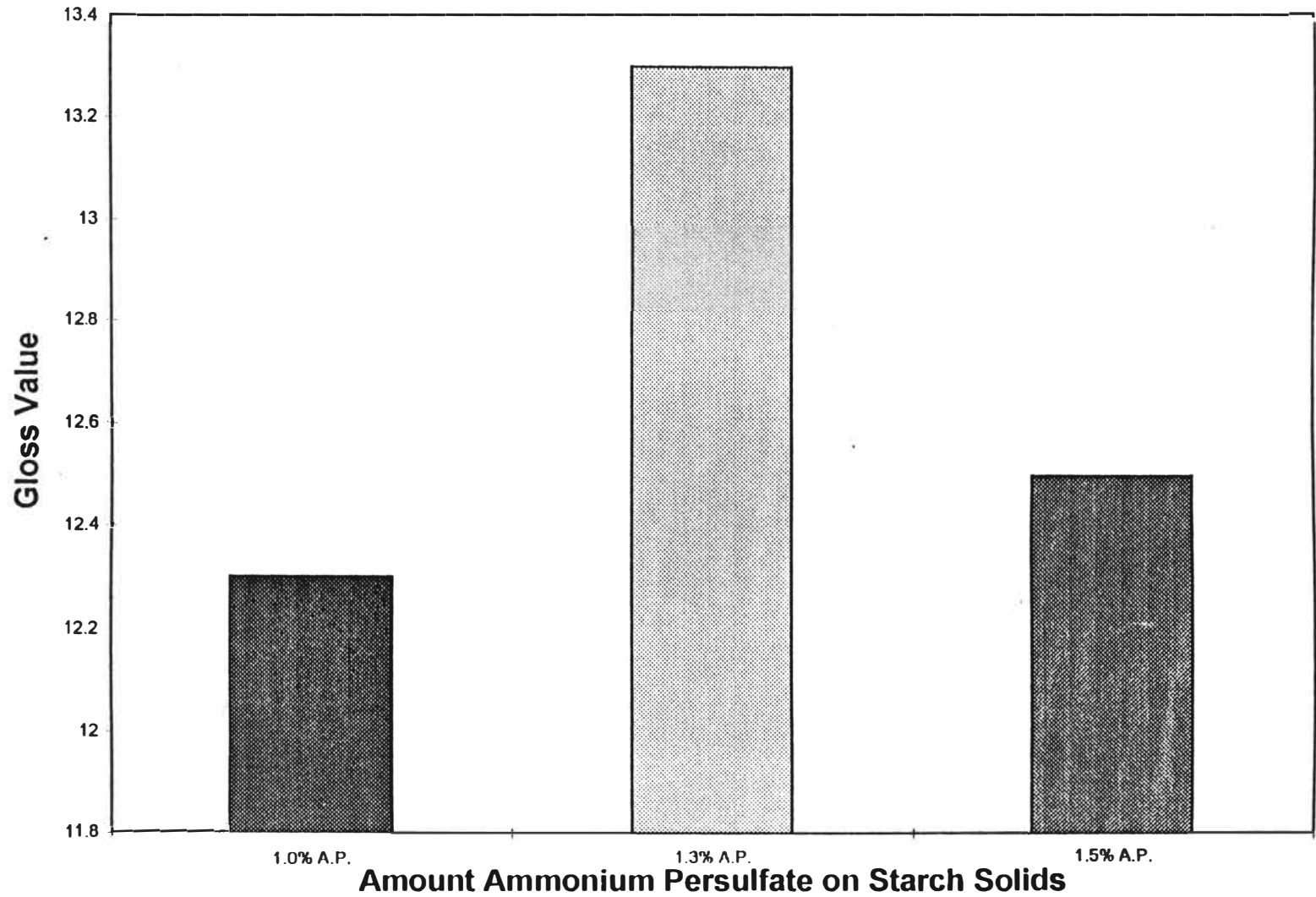


Figure13

Calendered Gloss (11.96 g/m² coat weight)

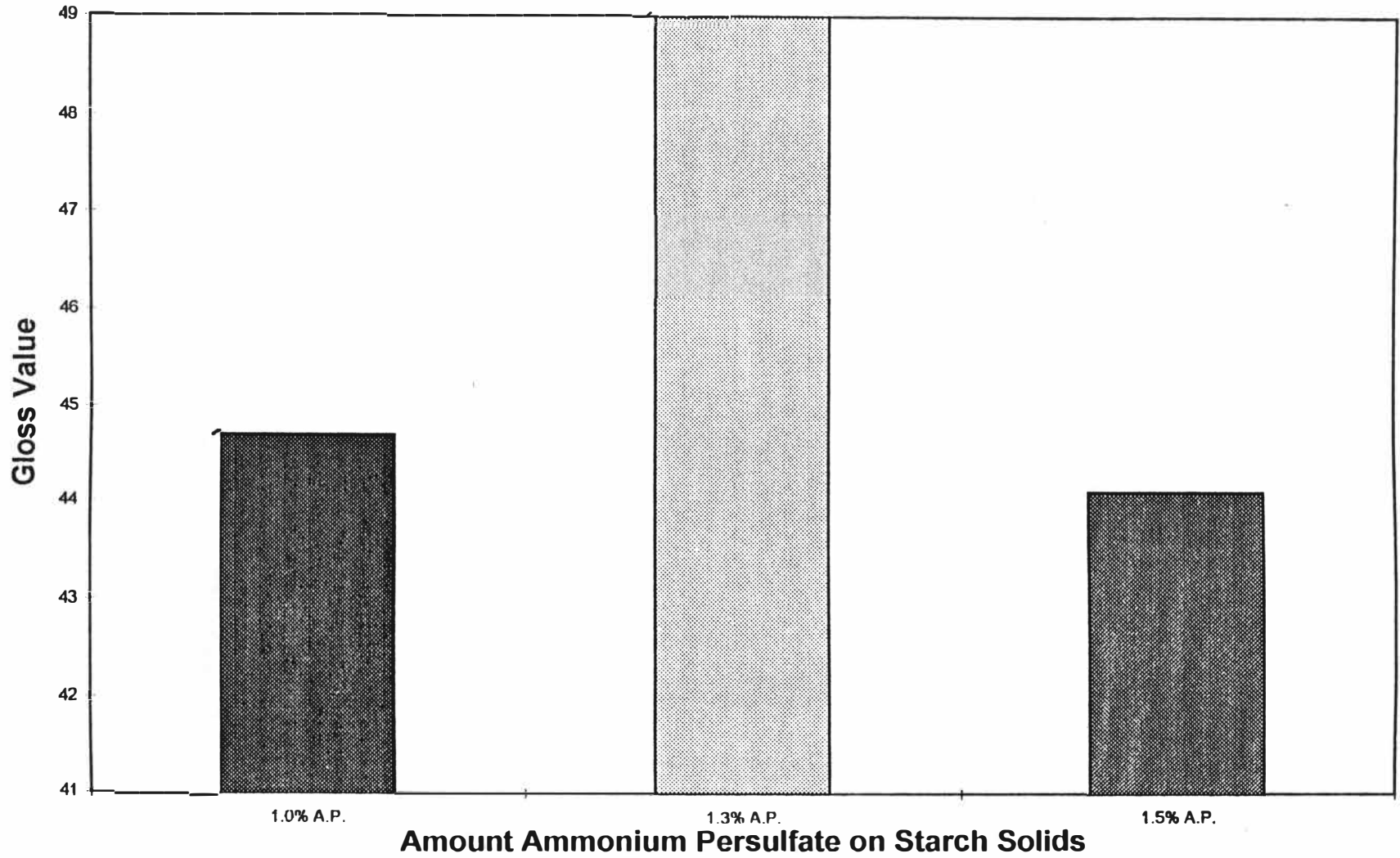


Figure 14

Uncalendered Wax Pick (11.96 g/m² coat weight)

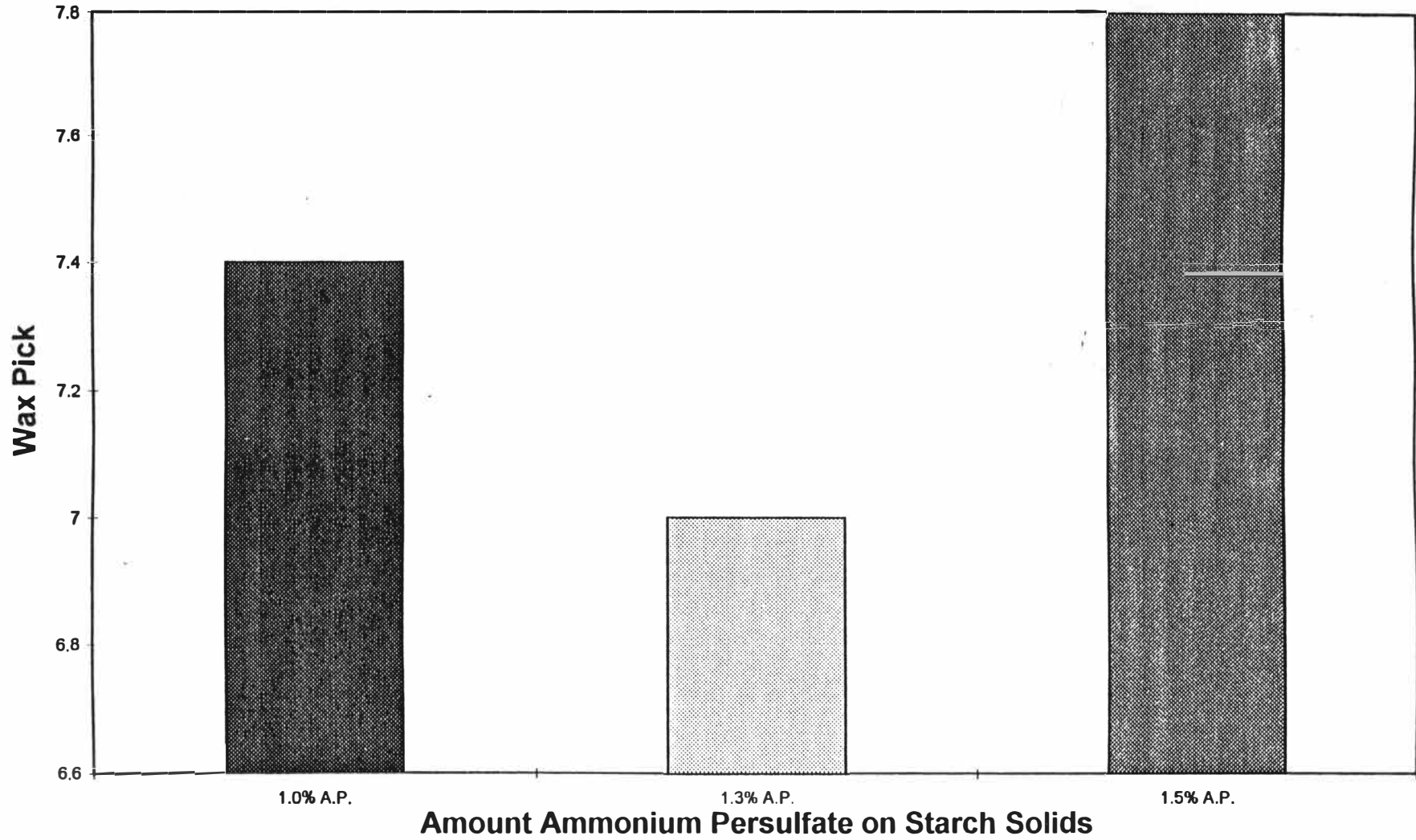


Figure 15

Calendered Wax Pick (11.96 g/m² coat weight)

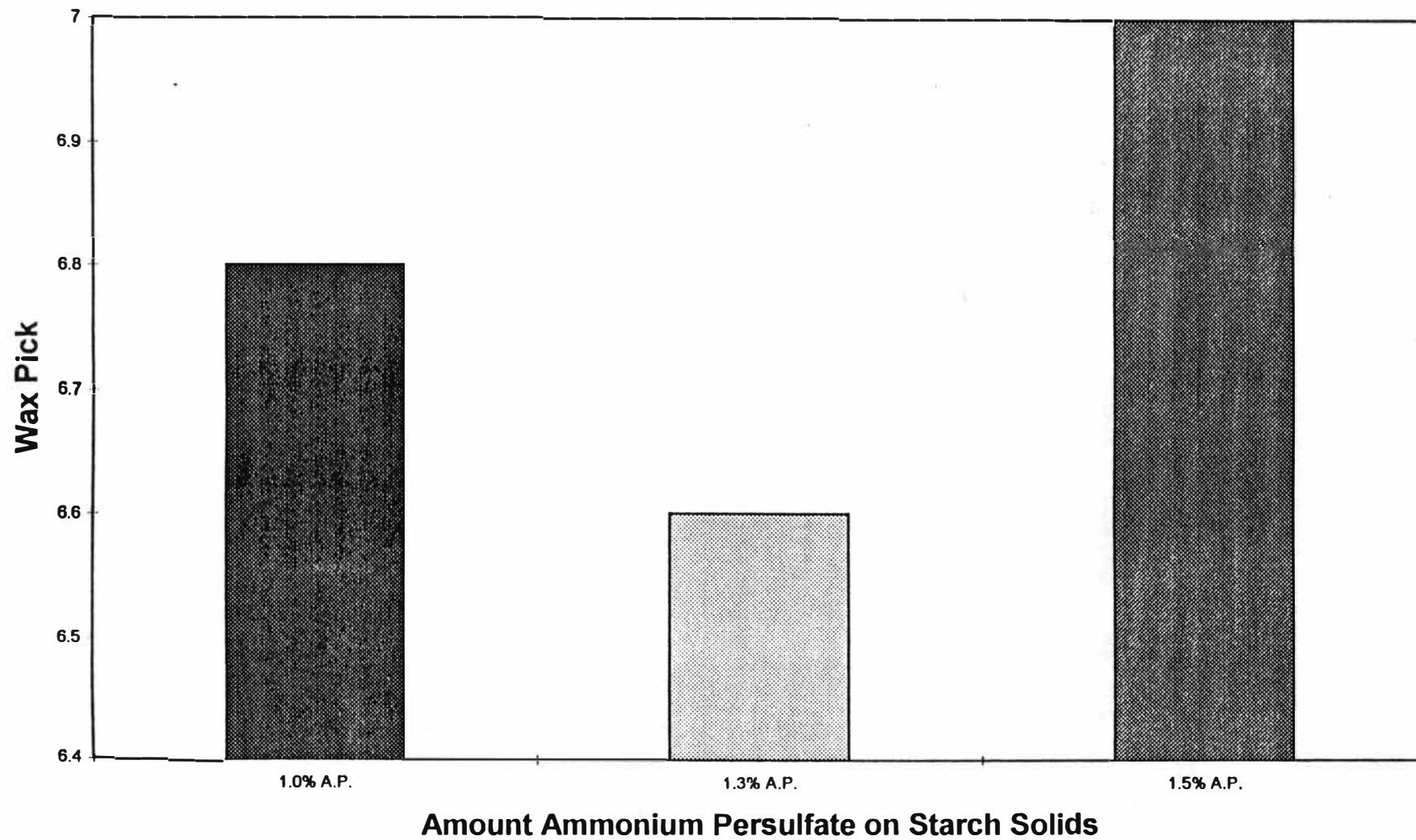


Table 1

WESTERN MICHIGAN UNIVERSITY CLC LABORATORY

TRIAL FOR RON ENGLEHART'S THESIS 11/30/95

2000 fpm factor = 78.941

0.018 CB

0.025 BB

0.50 SX

Trial ID	Run #	Blade Run-in	Mic Reading	Raw Stock g	Coated g	Coat Weight g/m2	Base Stock g/m2
Zero Point		233					
MV	1	50	183	0.9871	1.0769	7.09	77.92
	2	30	203	1.002	1.0651	4.98	79.10
	3	20	213	0.975	1.1194	11.40	76.97
	4	10	223	0.9921	1.4194	33.73	78.32
	5	17	216	0.9977	1.1492	11.96	78.76
	6	15	218	0.9788	1.1977	17.28	77.27
HV	1	15	218	0.9819	1.1365	12.20	77.51
	2	12	221	0.9915	1.2552	20.82	78.27
	3	13	220	0.9975	1.2198	17.55	78.74
	4	28	205	0.9999	1.0955	7.55	78.93
LV	1	28	205	0.982	1.1003	9.34	77.52
	2	32	201	0.9742	1.075	7.96	76.90
	3	18	215	0.9847	1.133	11.71	77.73
	4	15	218	1.0027	1.1679	13.04	79.15
	5	13	220	0.9789	1.1931	16.91	77.28

Table 2

Uncalendered Sheet Properties

<u>Percent (A.P.)</u>	<u>Brightness (%)</u>	<u>Smoothness (microns)</u>	<u>Gloss (%)</u>	<u>Wax Pick</u>
1.0	82.3	6.39	12.3	7.4
1.3	81.7	5.81	13.3	7.0
1.5	81.6	6.40	12.5	7.8

Calendered Sheet Properties

<u>Percent (A.P.)</u>	<u>Brightness (%)</u>	<u>Smoothness (microns)</u>	<u>Gloss (%)</u>	<u>Wax Pick</u>
1.0	80.4	2.12	44.7	6.8
1.3	80.5	1.98	49.0	6.6
1.5	80.2	2.24	44.1	7.0

Table 3

	(a)	(b)	(c)=[(a/b)x100]
	<u>Parts per 100 parts pigment</u>	<u>Solids Content % w/w</u>	<u>Wet Weight</u>
#2 Clay	100	72.2	138.4
Binder	15	25.8	58.4
Lubricant	1.0	50	2
<u>Dispersant</u>	<u>0.3</u>	<u>40</u>	<u>0.75</u>
Total Dry Wt.	116.3		Wet Wt. 199.6

for 55.3% solids: $116.3/x = 0.553$; $x = 210.3$ grams

Therefore, the water to add is $(210.3-199.6) = 10.41$ grams water

Discussion:

The first result was the effects of ammonium persulfate level on the viscosity of the starch slurries. It was found that at increased levels of ammonium persulfate there was very little to no change in the viscosity of the starch slurry. The predicted result would indicate a decrease in starch viscosity at increased levels of A.P. Reasons for the discrepancy are easily explained. Out-going temperature of starch slurry was 170 degrees at which the viscosity was immediately taken. A more accurate portrayal of the starch viscosity would have been obtained had the slurry been cooled beyond the retrogradation point and tested for viscosity. Also, due to jet cooker limitations it was not possible to decrease the A.P. levels any lower. It is possible that the amount of A.P. was too high to begin noticing changes in the starch viscosity.

It was apparent that the coating weights were easy to achieve in a highly controlled manner (refer to Table 1). This has a great deal to do with the dewatering characteristics of starch binders. The favorable runnability achieved with starch is in line with the low dewatering value. Excellent water retention of starch seems to compensate for relatively high high-shear rates (10). This also improves the blade runnability as colors with high dewatering tend to have detrimental affects (10).

The results obtained were all interpolated using the three coat weights run at different run-in levels on the CLC coater. The coat weights were targeted at 17, 12 and 7 grams/m². Graphs of these results were interpolated to achieve a coat weight of 11.96 grams/m².

The first result discussed was that of coating viscosity, Fig.7. It was noticed that as the content of ammonium persulfate in the starch slurry increased the final coating color Brookfield viscosity increased. Keep in mind the pH's of the 1.5, 1.3 and 1.0% A.P. levels were 2.1, 2.3 and 2.5 respectively. Because the pH of the starch slurry was not adjusted prior to the mixture into the coating color, initial shock was noticed. As the low pH starch was contacted with the 6.5 pH clay a rapid change in viscosity was noticed. The coating color became very viscous. Upon the addition of NaOH it was possible to bring the coating color pH to a level between 7.2 and 7.5. The addition of NaOH, though the addition did increase with increased levels of A.P., was not enough to overcome the initial shock which had been bestowed on the coating color. The low pH starch has a profound affect on the viscosity of the coating color due solely on its effect upon the viscosity of the fluid portion of the suspension (9). Corn starch is known to have high levels of fats, oils, and proteins. These materials react with starch during and after cooking, forming insoluble sludge. This material interferes with starch application, viscosity control and severely affect the end quality (8). The amount of acid produced and NaOH to neutralize the pH magnify the production of these insoluble sludges. Dispersion of the coating color may also play an important role in the coating color viscosity. A dispersing agent was added to the coating color. It appears that the best dispersion is in the lower viscous fluids where proper avoidance of flocculation was achieved. The effects of increased NaOH may have detrimental effects on the reaction of the dispersion reagent, thus causing increased viscosity.

The second result to be discussed is that of brightness, Figs. 8 and 9. In the uncalendered graph the effect of lower levels of A.P. increased the sheets brightness. During the process of converting the unmodified starch high levels of sulfuric acid are produced accounting for the decrease in pH. In this case the pH of the starch was not initially as low as the others. Therefore, less NaOH was needed to raise the pH. Some difficulties are commonly associated with corn starch conversion. Corn starches have a protein inherently which may have detrimental effects on coating brightness (8). At lower levels of A.P. the protein and oils present in the starch go undisturbed, but as more NaOH interferes the results can be seen. The graph for calendered brightness shows 1.3% A.P. to have the highest brightness. The overall results show a decrease in brightness due to calendering. This is expected due to the increased gloss characteristic of the sheet. The particles tend to fuse into the base sheet putting a gloss to the sheet. The brightness meter picks this up as a dull sheen. The smoother sheet does not reflect the light back to the meter the way the uncalendered sheet had. The surface of the sheet has become more mirror like and has projected the angled light source away from the detection unit.

The next result to be discussed involves the smoothness characteristics of the sheets, Figs 10 and 11. To attain the performance needed, binder systems usually employ starch due to its low cost and coating solids are usually below 60%. Coat weights for light weight coated grades are always decreasing (1). The uncalendered and calendered smoothness of the sheet favored the 1.3% A.P. level. Smoothness is characterized by surface uniformity. If the starch slurry is too viscous it tends to cover peak deformities in the base stock. If the coating color is not viscous enough it will become pooled in void

deformities of the base stock. The goal is to find a happy medium. It appears that the 1.3% addition level is this medium. It is found that starch unlike other binders has a very low dewatering value, this results in a relatively high immobilization-solids level (10). This allows sufficient time for the starch to fill the void areas of the sheet and provide adequate surface uniformity. The sheet would tend to be less uniform had the dewatering effect resulted in incomplete transfer to deformities in the base stock. The poor smoothness characteristics of the other two A.P. addition levels can be attributed to the viscosities of the coating formulation. The calendered sheet exhibits much better smoothness as surface deformities are improved under the high pressure of the calender.

The surface uniformity characteristics also have a profound effect on the sheet gloss, Figs. 12 and 13. It is shown that the 1.3% A.P. level has the best uncalendered and calendered sheet. This is directly related to the surface smoothness. A more uniform sheet will be one in which the peaks and void deformities in the base sheet are covered with the coating color. As the coating color forms into and onto these spaces and peaks the smoothness and gloss characteristics are directly related. The gloss of the sheet involves the reflectance of light off the coated sheet and back to a detector. As the coating fills the void spaces the substrate becomes more mirror like. The light is therefore, reflected and transmitted directly to the detector. In the case of the other two substrates at differing levels of ammonium persulfate, good surface uniformity was not achieved. The light transmitted by the source was therefore scattered and less light was detected. The calendered sheet has considerably higher gloss due to improvement in surface uniformity caused by high pressure.

The next part of this discussion will deal with the wax pick or surface strength of the coating colors, Figs 14 and 15. It was found that the values for wax pick were within one standard deviation from one another, therefore, their differences were not significant. The values, however, show the exact opposite trends as compared to the smoothness and gloss. It has been proven that although starch provides the best runnability of all the binders due to its low dewatering capabilities, this has detrimental effects on the surface strength. It has been shown that dewatering of the coating has an inherent effect on the interaction between pigment and cobinder which must be controlled to provide smooth runnability (10). It was found that because of the high immobilization solids mentioned before some detrimental affects result in poor pigment binder interaction. This results in a compact coating structure and may thus contribute to the high gloss values (10). High surface strength, however, favors strong pigment interactions. Possible problems also results in the conversion process. Starch modification methods produce some water-soluble sugars and low-molecular weight starches which have poor film-forming and low-binding strength properties (2). Several other possibilities also exist. Over conversion of starch by thermal chemical processes has been shown to reduce the starches molecular weight and adhesive strength of the coatings (6). Lower adhesive strength could be due either to migration of the starch and/or reduced adhesive capabilities of lower molecular weight fractions (6). It is also said that increased machine speeds tend to cause starch migration to the surface of the sheet thus decreasing the interaction with the pigment particles and the base stock (6). All these reasons are quite possible explanations for the given wax pick values ranging from 6.4 to 8.

The final characteristic involves the relationship of the high-shear rheograms, Figs. 4, 5 and 6. All of the following rheograms suggest thixotropic effects. Thixotropy is manifested by catastrophic breaking of the internal structure in a suspension during the up curve and reforming on the down curve (12). Upon shearing, the fluid attains a state of lower potential energy due to the structural changes which depends on both chemical and hydrodynamic processes (12). The loop quantifies power loss during the continuous input of energy into the fluid sample undergoing testing and it is independent of the thermal effects (12). Thixotropy is defined as isothermal, reversible reduction in viscosity with shear rate (12). High-shear viscosity of the coating color is important in determining how the formulation will react under the shear forces present in the coating, pumping, and screening operations. Another important piece of information which is calculated in these graphs is the hysteresis area of the coating colors. Hysteresis is the amount of destruction that results from the exposure of high shear (12). As the area of hysteresis increases so does the amount of destruction to viscosity or fluidity. It was found that high levels of ammonium persulfate will tend to degrade the viscosity of the coating color at high shear forces. High levels of ammonium persulfate did, however, give the highest initial viscosity values.

Difficulties:

During the completion of this senior thesis a number of difficulties were encountered. Most of these difficulties were related to the runnability of the starch jet cooking unit.

The first difficulty encountered was not known at the conception of this thesis. It was found that the jet cooking apparatus was not capable for the complete conversion of this starch. Literature suggests that the retention time of starch in the holding coil is in the 5 to 7 minute range. This time was virtually impossible to achieve. The volume of the holding coil on the unit was 0.225 gallons, and the lowest allowable pumping capacity on the positive displacement pump was 0.1 gpm. This suggests a hold time of 2.25 minutes. This was hardly sufficient for the full conversion of the starch. It was, however, recorded that the actual hold time of the starch in the coil was 3.25 minutes. According to reference (14) this is sufficient time to convert the starch.

Another problem was encountered when trying to achieve the target outgoing solids of 25%. It was found that entering with a solids level of 32% was not high enough. Flashing of steam and the addition of quench water to the process decreased the outgoing solids nearly 30% to a low 22.5% outgoing solids. This was acceptable considering a 55.3% coating solids was possible.

The hand control to control back pressure was also in question. Severe changes in the back pressure throughout the run of starch caused indeterminable variances in the retention time. This resulted in periods of high and low solids flow exiting the unit.

During preliminary trials using the jet cooker some problems were connected that eventually resulted in better runnability of the jet cooking apparatus. It seems that prior to the use of this instrument for this thesis fouling of the sensors and deposits in the coil created back pressure fluctuations and eventually caused the unit to plug with unmodified starch. The unit was dismantled and unplugged using high pressure air and 5% caustic solution. The coil was reinserted into the unit and it was again flushed with a caustic solution. In doing this the fouled sensor and coil deposits were removed.

One of the constituents produced in the thermal conversion process is sulfuric acid. This created very low pH values in the coating slurries. This required large amounts of NaOH to be added to the final coating color to get it to a runnable pH level.

Finally the starch viscosity levels were not as predicted. Due to limitations running the thermal cooker, very high amounts of ammonium persulfate were required. The need for higher levels produced low viscosity starch slurries. It was found that all of the starch dispersions had a relatively low viscosity of 50 Cp at 100 RPM and 170 degrees Fahrenheit.

Conclusions:

It was found that the thermal jet cooker in the Western Michigan University Pilot Plant did not have the capabilities to run unmodified starch. The retention time of the holding coil limit the device to conversion of premodified starches. Instabilities in the flashing of steam and starch and the flow of quench water into the system create difficulties when trying to achieve 25% outgoing solids. A dilution of 30% on average was noticed bringing an ingoing 32% solids slurry down to an exiting 22.5%. Limitations of the jet cooker also made it impossible to provide ammonium persulfate levels comparable to industry standards. The amount of ammonium persulfate was quite high and resulted in indistinguishable exiting starch viscosities. The results of high shear viscosity did, however, show the expected results.

It was found that the coating trials on the CLC coater where fairly easy to run. The three target coat weights of each coating color were readily achieved. The reason for this ease of control has to do with the low dewatering effect which is inherent to corn starch. High dewatering effects the blade runnability and control causing detrimental effects to the finished sheet. This tendency is avoided when using starch as a binder.

It was found that the amount of ammonium persulfate present had significant effects on the coating color viscosities. The higher the amount of ammonium persulfate the higher the coating viscosity. The starch slurries were not adjusted to pH prior to entering the coating color. As the 2.1 -2.5 pH starch slurry contacted the 6.5 pH coating clay a shock caused increased viscosity. The low pH starch interacts with the fluid phase of the coating color, thus creating the dramatic increase in viscosity.

Properties such as brightness, smoothness and gloss favored the 1.3% ammonium persulfate based on starch solids level. This level created the mid-range coating color viscosity. This suggests that the in the medium viscosity coating starch migrated into the base sheet lowering the shrinkage and increasing gloss and smoothness. The high gloss values can be attributed to the high immobilization solids of the starch coating colors. This results in poor pigment binder interaction, but causes a compact coating structure contributing to the high gloss.

There were not significant differences of wax pick values at varying levels of ammonium persulfate. Starches during thermal conversion produce low molecular weight starches and insoluble sugars which cause detrimental effects in binder pigment interaction. Over-conversion and migration of binder to the surface of the sheet or into the base sheet will reduce adhesive strength. The low dewatering effect also has detrimental effects concerning pigment binder interactions.

The results of high shear support literature about starch binders. It was found that all of the coating colors gave a thixotropic rheogram, which is supported in the literature. Thixotropy is the isothermal, reversible reduction in viscosity with shear rate. It is important to include these characteristics to show how the coating colors would react in the presents of high shear such as that present in coating operations, pumping, and screening. It was found that at increasing levels of ammonium persulfate the result was decreased area of hysteresis. This causes a decrease in the destruction of the initial coating color viscosity in the presence of high shear rates.

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