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Use of Brazilian Clays for Coating Formulations

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"USE OF BRAZILIAN CLAYS FOR COATING FORMULATIONS"

by

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PREFACE

The following work deals with the investigation of a Brazilian Clay originated in Espera Feliz, Minas Gerais for the sole use as a pigment in coating formulation. The laboratory work was carried out using the installations of the Paper Science and Engineering Department at Western Michigan University. The major finding was that the clay, as it is available today in the market, can not be used for an acceptable final product.

ACKNOWLEDGEMENTS

I would like to thank the Industria Fabricadora De Papel in the person of Dr. J. Karmann who made available the sample along with informations. Also I would like to thank Professor J. V. Valarelli from the Department of Geology of the University of Sao Paulo, who furnished a complete analysis of the sample.

FOREWORD

The massive effort of the Brazilian Government to develop a stronger and more competitive industry has boosted the production of pulp and paper up to six times its level of 1969.

The increasing demand for coated papers has forced the industry to look for new domestic sources of clay and to try to use the internally available product. Besides the undesirable situation of dependency upon a source many thousands of miles away, the difference in cost is the most appealing factor of all.

Today the three largest pulp and paper producers in Brazil have their own mines to assure a reasonable product and continuous supply, it is up to the paper industry to develop the resources and necessary technology.

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INTRODUCTION

Kaolin or china-clay, is a substantially white mineral consisting largely of Kaolinite which is a hydrated-aluminum silicate, $Al_2O_3 2SO_2$ $2H_2O$ with the following composition:

Al_2O_3	39.5%
SiO_2	46.5%
H_2O	14.0%

Filler grades are usually mined from local deposits. For coating grades most of the world supply comes from two areas: Georgia and Southwest England. British clays are of primary deposits, i.e., they are mined at the place of formation. Georgia deposits are secondary or sedimentary, meaning that they have been washed from their place of origin and deposited someplace else.

The high cost of transportation and the undersirable dependency upon resources thousands of miles away have driven the industry to try to replace imports with locally produced grades. In Brazil where old geological formation predominates, clay has been mined, so far, for use in paper filler grades, rubber, etc. where the quality is not as critical as for coating clays.

When producing coating grades the need for a much more uniform, higher brightness, and better particle size distribution requires a better control from the time of extraction through the process which may require some

additional steps in beneficiating the mineral.

Water washed process is the only one used so far for coating grades due to the degree of sophistication that it offers and its versatility. Air flotation, so far, is only used for filler grades. The steps required in the water washed process in general are, dispersion of the crude Kaolin, screening with a 200 mesh for removal of grit, fractionation using gravity or centrifuges for removal of coarser particles to control the end product's particle size distribution. For some grades delamination, bleaching and beneficiation using ultra flotation are required (12).

PHYSICAL PROPERTIES

Brightness

Tappi Standard T 646 M-54 is a comparative measurement of light reflectance at 457 nanometers considering MgO as 100%. Color in clays are mostly affected by three factors; presence of iron oxide on the surface of the Kaolin crystal, presence of titaniferous compounds and particle size distribution.

When fractionation is used to produce a coating clay, brightness is improved slightly for each fractionation step and the gross fraction can even have a lower brightness than the starting minerals (8).

Bleaching as a next step for improving color is often used. The clay surface in the crude mineral is stained with oxidized iron compounds. After the slip have been fractionated, it is flocculated with H_2SO_4 to a low pH, under which conditions, the iron compounds are more soluble and decoloration and removal of the iron oxides are done more easily. The actual bleaching is done with a strong reducing agent as zinc hydrosulfite with its potential increased by the low pH of the system. The reaction is rapid with increases up to 7^o GE reported (6).

The reagent, zinc hydrosulfite, is commonly produced at the site with costs reduced to half of the cost of the zinc hydrosulfite powder marketed.

Sedimentary deposits in Georgia had a lower brightness than English clays. American clays have its color limited to a maximum of $86\text{-}87^o$ GE after being bleached. The cause of this limited brightness is a titaniferous

compounds that makes up to 2% giving a cream color to the product.

Froth flotation as it is, is limited to grains larger than 40 microns. Smaller particles would require a smaller bubble size and this would bring along problems with emulsification and therefore flotation itself.

In the early sixties more work on flotation brought the development of the concept of pigback carriers. Using minerals with sizes around 40 microns that would be pretreated to be selective to a determined particle. This process then became known as ultra flotation and has been used exclusively in the mining industry (8).

For the clay industry this process made possible the production of high quality clays with 93% of the particles finer than two microns and 90+ brightness. The carrier used for Georgia clays is ground limestone. Requirements of the order of 400-800 lbs of limestone per ton of feed is reported by Minerals and Chemicals Phillipp. Recycling and/or recovery of the carrier can be used and it is a matter of cost.

Particle Size and Shape

The Kaolin particle shape is an irregular hexagonal plate. The ratio diameter to thickness is 12:1 and in nature these plates appear also in stacks. The plates bear a negative charge on the faces and a positive charge on the edges. Dispersion is accomplished having an alkaline medium and in aqueous solutions a particle of Kaolin presents a typical double layer charge. Further dispersion of the particles is achieved by adding

to the system electrolytes. Different electrolytes would give varying degrees of deflocculation. Asdell in his works covers the subject of clay dispersion quite broadly.

By applying shear to clay systems of high concentration, stacks of plates, or sometimes called booklets, can be broken down into individual plates. When done by the clay producer the final product is designated delaminated clay.

The Kaolinite crystal presents, according to the structure work out by Gruner alternated layers of silica and alumina bonded together through oxygen and hydroxyl valence linkages. A natural cleavage plane appears at the weakest point in the structure which is the silica hydroxyl secondary valence bond. A fracture in this plane will not break primary valence bonds and unsaturation does not occur. On the other hand, cleavage perpendicular to this plane will yield active areas on the crystal which in water systems will attract hydroxyl groups taking along H_2O of hydration. This therefore explains the diffuse double layer and the crystal will be negatively charged acting as a negative ion having a limited capacity for base exchange. The clay will adsorb positive ions to balance its charge and this is how electrolytes impair a high degree of deflocculation.

Viscosity and Coating Surface Properties

The steps of fractionation and delamination when processing clays will determine two very important characteristics of clay colors, namely, viscosity and coating surface properties. Clays can be assumed to have its

fraction of larger particles made of stacks and the fraction of small particles of platelets.

When preparing coating colors, there will usually be some delamination done when shear is applied to achieve a high degree of deflocculation.

Water clay systems are very complex and do have many factors influencing viscosity. When in a flocculated state a clay water slurry shows a yield value and a very much characterized thixotropic flow. When deflocculated to its minimum viscosity the flow changes to an almost Newtonian. With increase in solids concentration, close to the point of critical volume, dilatancy occurs. It has been reported by Asdell a maximum of 73% solids, or 51.5% by volume, as the critical point for a clay with 84% below two microns equivalent spherical diameter.

In a deflocculated system the smaller the particle size the higher the viscosity of the system.

Besides the problems posed by viscosity which is directly related to particle size and shape, the final appearance and surface quality of the coating are also a function of the size and shape. At this point it must be understood that for all practical purposes all particles of large size are made of stacks.

Hecklau and Pavol determined in their works that besides some interaction between clay and adhesive shown in the viscosity, the surface properties of ink hold-out and gloss were definitely mostly affected by fineness of the clay.

At this time it should be mentioned that adhesive demand is less for fine clays, but water held within the film increases sometimes posing problems to drying on web offset presses.

Better coverage or a more opaque film can be obtained with colors made of finer particles.

SAMPLE CHARACTERIZATION

The sample used in this work was furnished by Industria Fabricadora de Papel, a producer of fine papers. The clay was extracted in a mine owned by the group in Espera Feliz, Minas Gerais. For certain grades of paper, mixtures of up to 30% of this clay can be tolerated with Georgia's delaminated clay, and then only with delaminated clay.

After being mined, the clay undergoes the following steps of beneficiation: dilution, addition of dispersant; sand removal by sand traps; flocculation with alumina; decantation and drying.

A sample of the clay was sent to the Department of Geology of the University of Sao Paulo to determine its chemical composition and below are the results set aside a typical analysis for Number 2 clay from Georgia.

	BRAZILIAN	GEORGIA'S NO. 2
SiO_2	44.6 %	44.32 %
Al_2O_3	41.43%	39.42 %
TiO_2	traces	1.29 %
CaO	traces	0.68 %
MgO	traces	0.21 %
Fe_2O_3	0.07%	0.67 %
Firing Loss	15%	13.95 %

pH

Using a glass electrode, a pH of 3.8 was determined in a sample of 10 g of clay in 100 ml of distilled water with the clay still in suspension.

Brightness

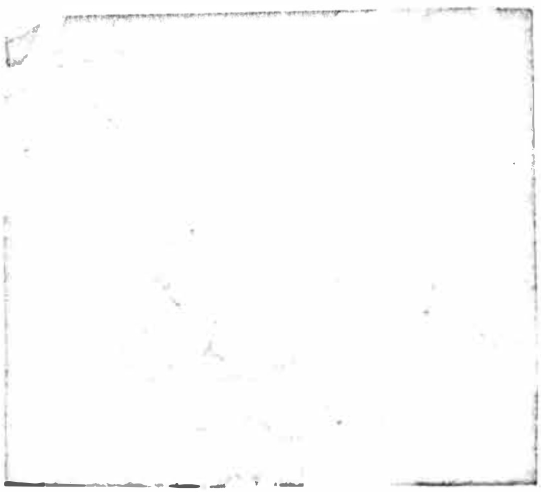
Using the hardward from the Elrepho Brightness Meter we found that the sample from Brazil had a fantastic value of 85.9% while the sample of No. 2 from Georgia had only 79.8%.

Particle Size Distribution

Using the method of gravity bottle applied to Stokes law we determined the particle size distributed in terms of equivalent spherical diameter. Graph one displays the results along with a typical no. 2 clay.

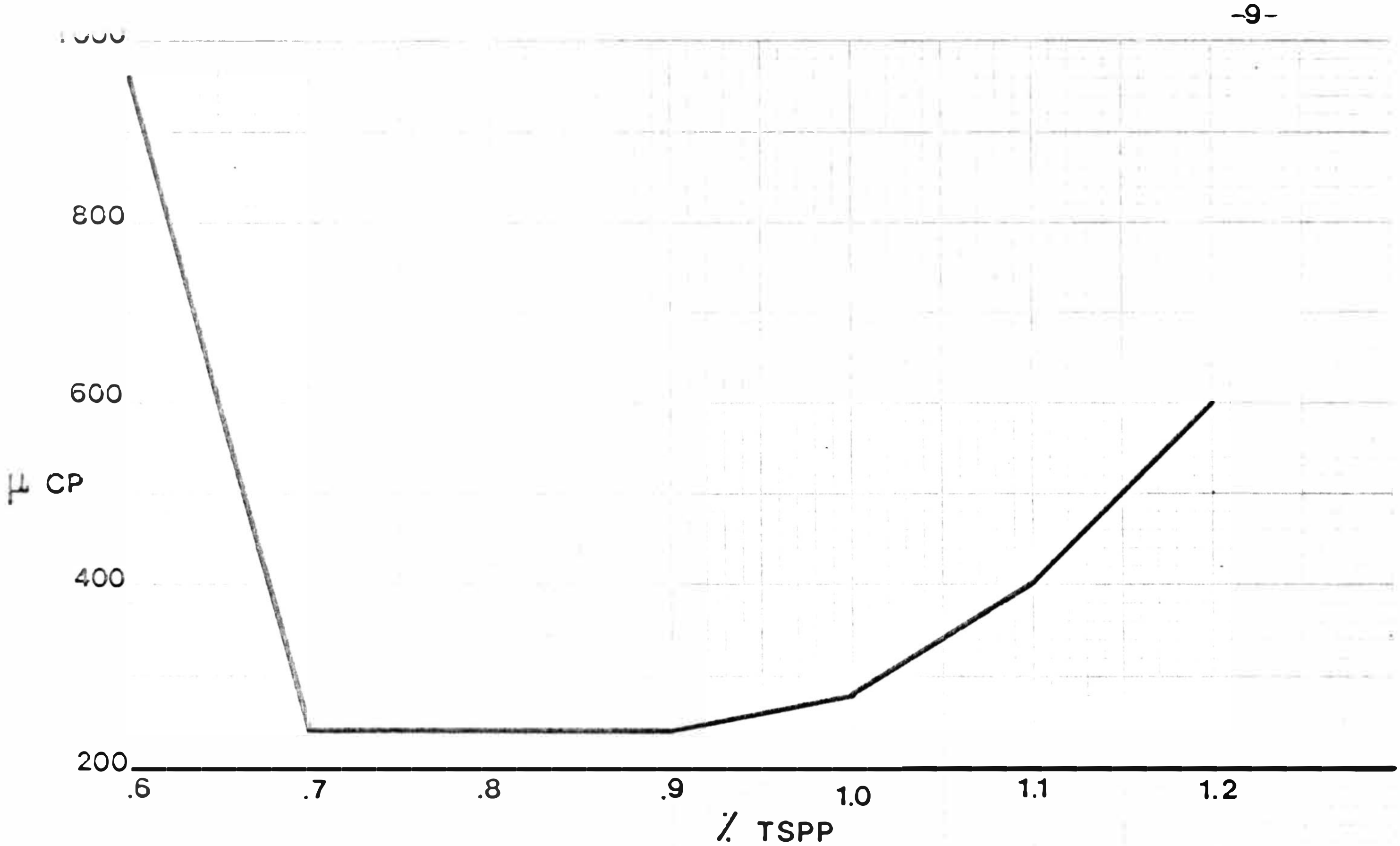
Grit Mesh 325

A 2% residual in mesh 325 was found and the result included in the particle size distribution graph as of larger than 40 microns particles. A photomicrograph was taken to show the amount of hallosite present in the Brazilian sample and in photo (1) it can be easily identified as the needle shaped particles.



BRAZILIAN

NO.2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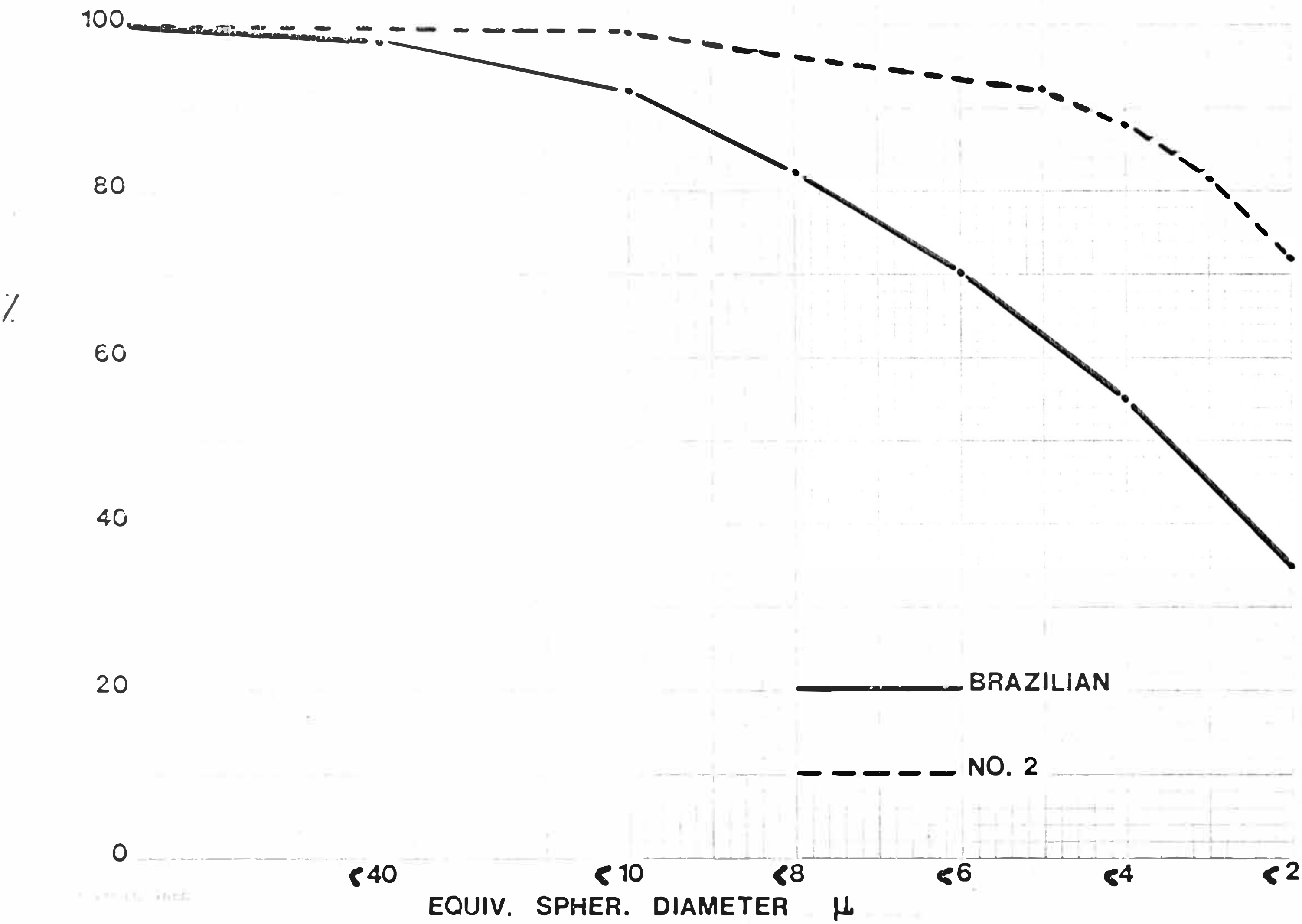
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EQUIV. SPHER. DIAMETER μ

EXPERIMENTAL PROCEDURE

Preparation and Application of Color Slip

Dispersion

When preparing the color the first step was to determine the amount of dispersant required for lowest viscosity. This was done by using the Brookfield Viscometer and the dispersing agent T.S.P.P. It was found that 0.8% of T.S.P.P. gave maximum dispersion, (Graph 1). The predispersed No. 2 was assumed to be at its maximum dispersion.

Adhesive and Solids

Twenty parts of latex, Dow 328, per hundred of clay were added to the slip in the sigma mixer after 30 minutes of mixing at higher solids. The final solids were for both clays 65%.

Rheology

Hercules viscosity curves were run and, as expected from the particle size distribution curves, the Brazilian clay showed a much lower viscosity; approximately one-half of the No. 2 clay which was blocking at 0.82 poises as shown by curve (3) from the Hercules viscometer.

Application on the Keegan Coater

As base stock a low brightness paper was used so that the final product evaluation would be easier. Four different size Mayer rods were also used so that coat weight could be overlapped. Different coat weight was expected due to different viscosities. When applying the coating no problems were encountered except the blocking of No. 2 clay at the rod.

EVALUATION OF THE FINAL PRODUCT

The following tests were run on both coated papers made and on the base stock.

Coat Weight

The basis weight of the raw stock and coat weight was determined by average values. The use of four different rods, numbers 8, 10, 14, 18 gave us coinciding amounts applied so that comparison became easier (Graph No. 4).

Opacity

In determining the gain in opacity after the coating was applied a Bausch 8 Lomb Opacimeter was used. The results can be seen on graph No. 4 and Table 1.

Smoothness

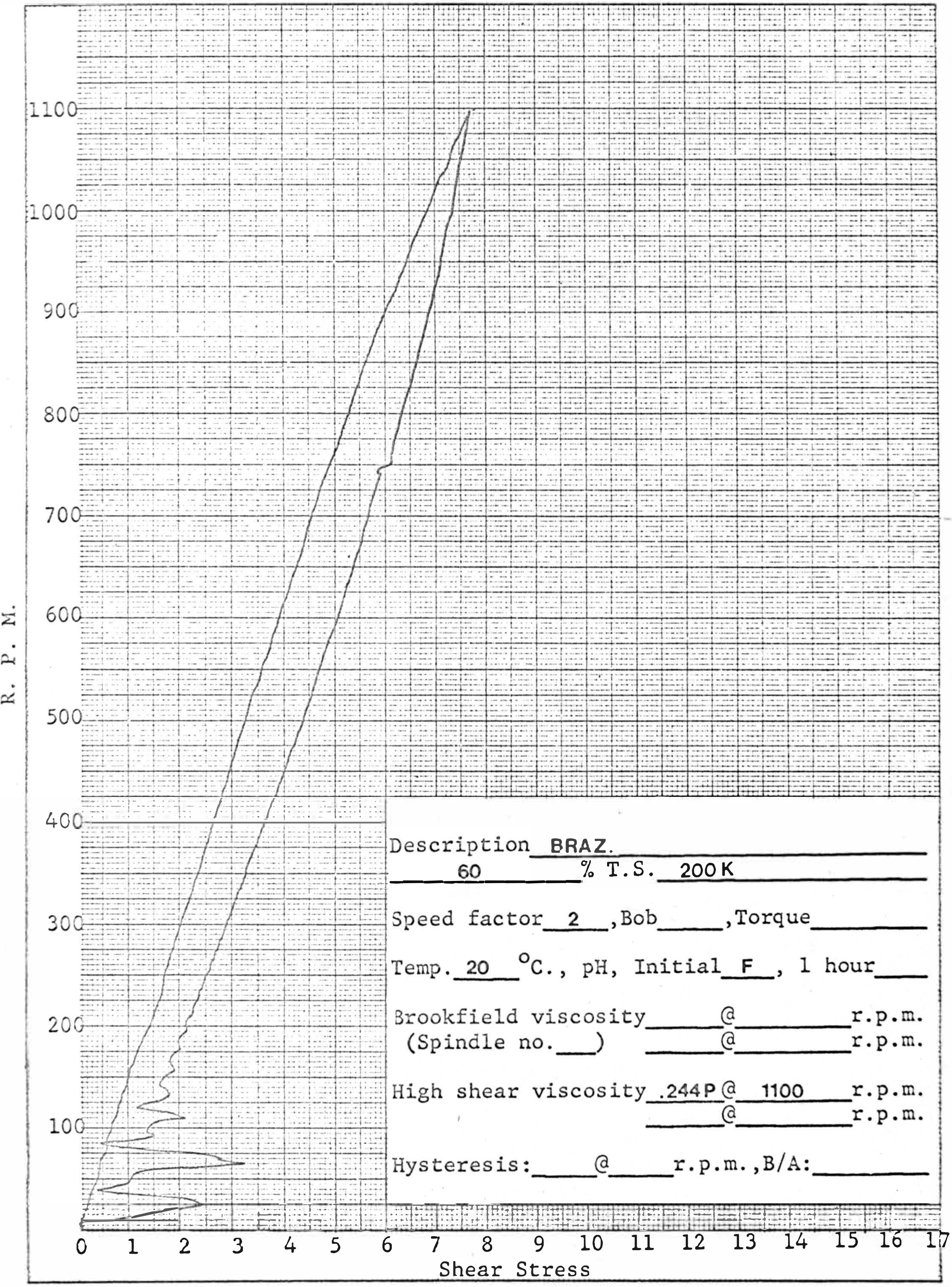
The Sheffield Smoothness test was used and the smoothness values recorded as cubic centimeters of air per minute. Results in Table 1 and Graph No. 4.

Brightness

The Martin Sweets Instrument was used and the results are also tabulated in Table 1 and Graph 4.

Analysis of Results

The presence of grit (sand crystals) and large clay particles may be the most important factors in the low value of opacity presented by the final coating. Since our base stock was of low brightness this may have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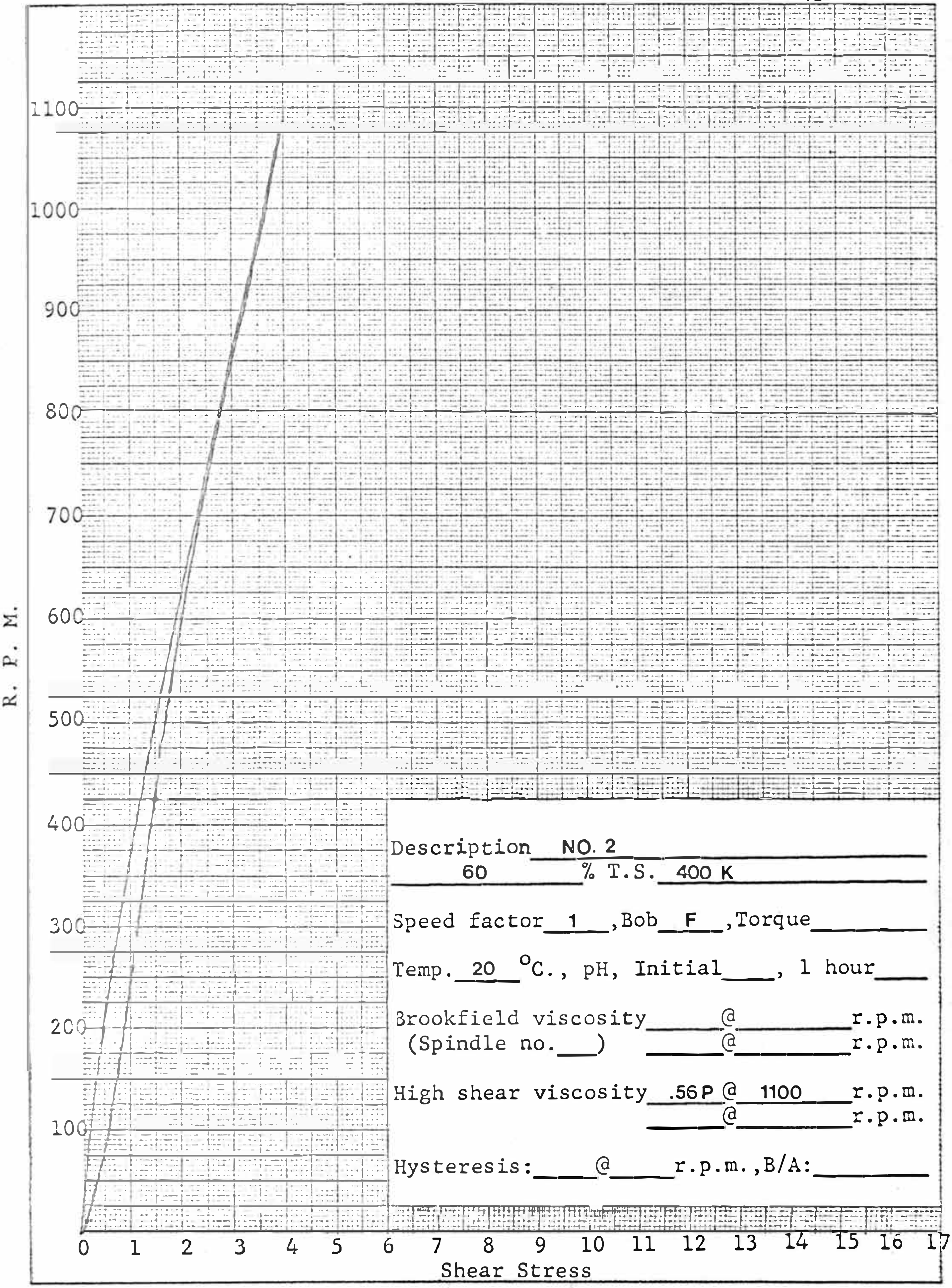
16
17
Shear Stress
Description BRAZ.
60 % T.S. 200 K
Speed factor 2 ,Bob ,Torque
Temp. 20 °C., pH, Initial F , 1 hour
Brookfield viscosity @ r.p.m.
(Spindle no.) @ r.p.m.
High shear viscosity .244P @ 1100 r.p.m.
@ r.p.m.
Hysteresis: @ r.p.m.,B/A:



Description NO. 2
60 % T.S. 400 K

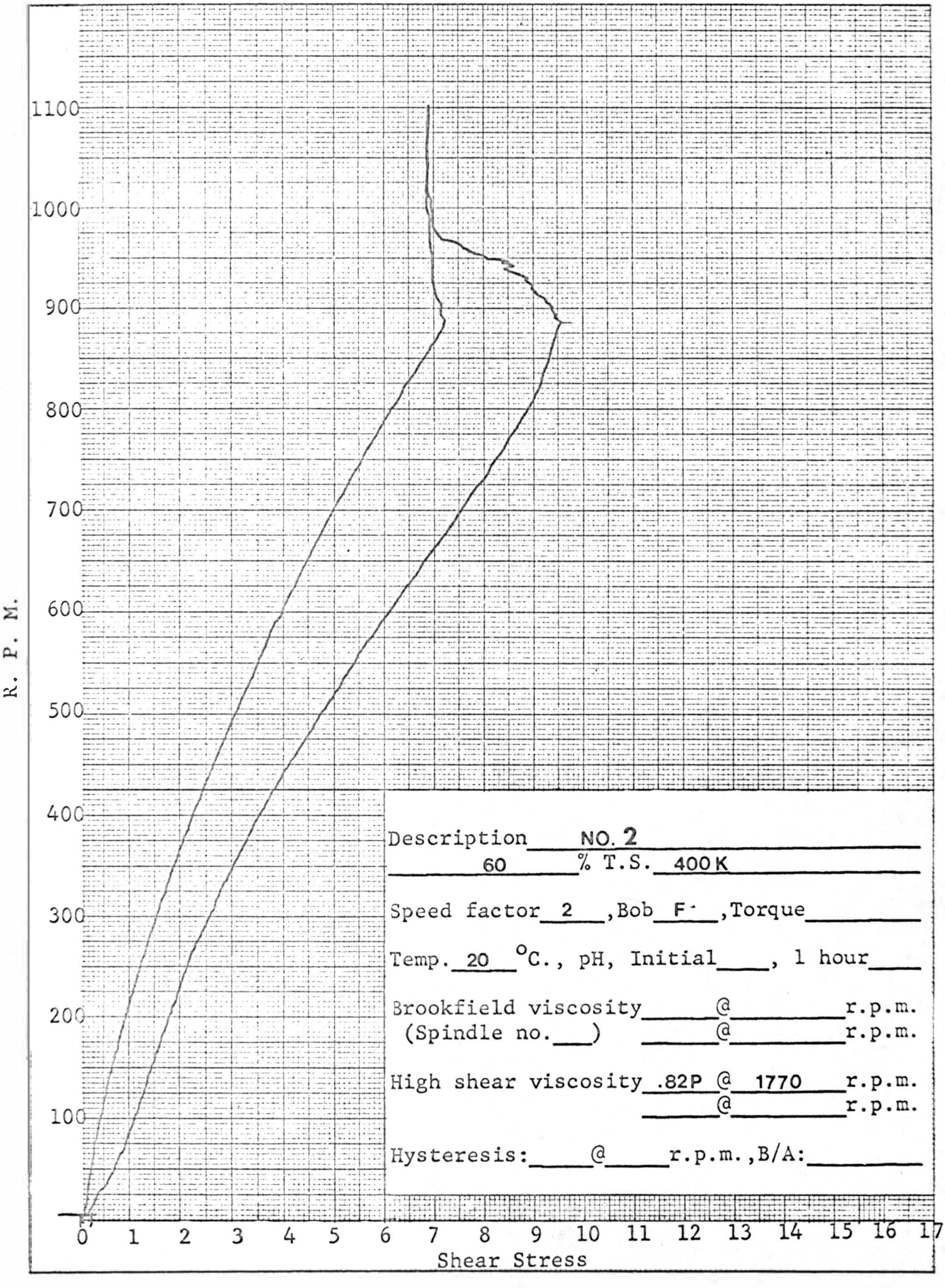
Speed factor 1 , Bob F , Torque ____

Temp. 20 °C., pH, Initial ____, 1 hour ____

Brookfield viscosity ____ @ ____ r.p.m.
(Spindle no. ____) ____ @ ____ r.p.m.

High shear viscosity .56 P @ 1100 r.p.m.
____ @ ____ r.p.m.

Hysteresis: ____ @ ____ r.p.m., B/A: ____


R. P. M.
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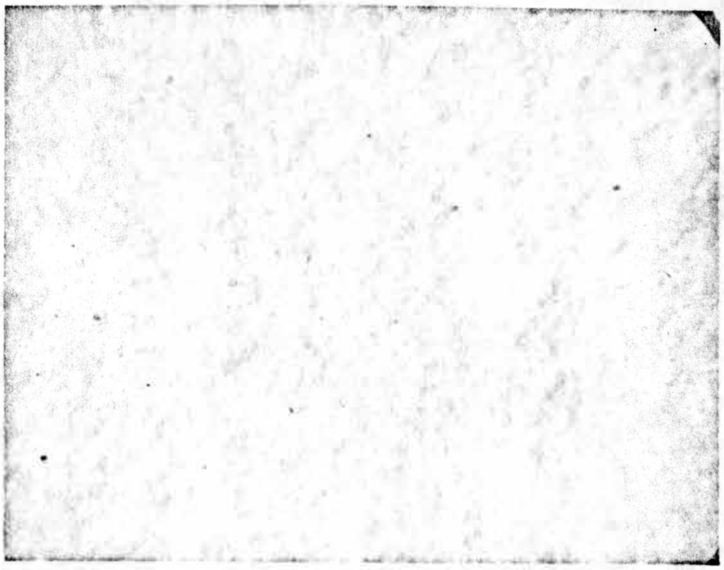
Shear Stress
Description NO. 2
60 % T.S. 400 K
Speed factor 2 ,Bob F ,Torque
Temp. 20 °C., pH, Initial , 1 hour
Brookfield viscosity @ r.p.m.
(Spindle no.) @ r.p.m.
High shear viscosity .82P @ 1770 r.p.m.
@ r.p.m.
Hysteresis: @ r.p.m.,B/A:

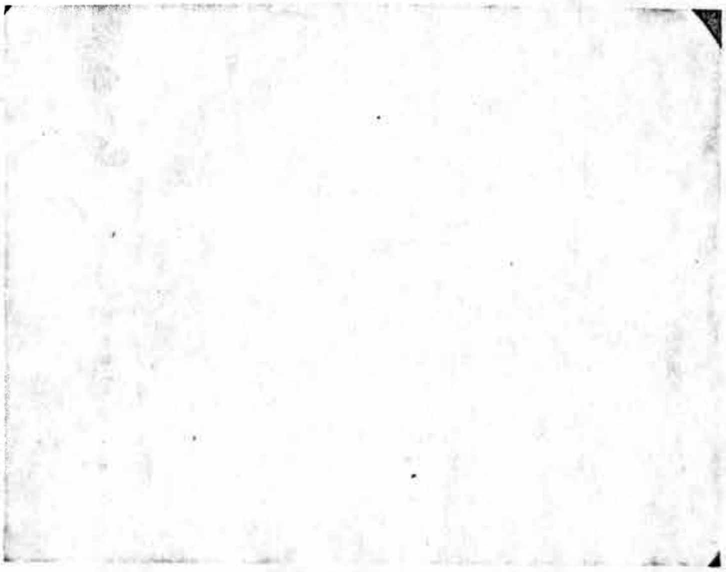
BRAZ 44X LOW ANG. ILUM.

NO 2 44X LOW ANG. ILUM.



BRAZ 88X LOW ANG. ILUM.

BRAZ 88X TRANS. LIGHT



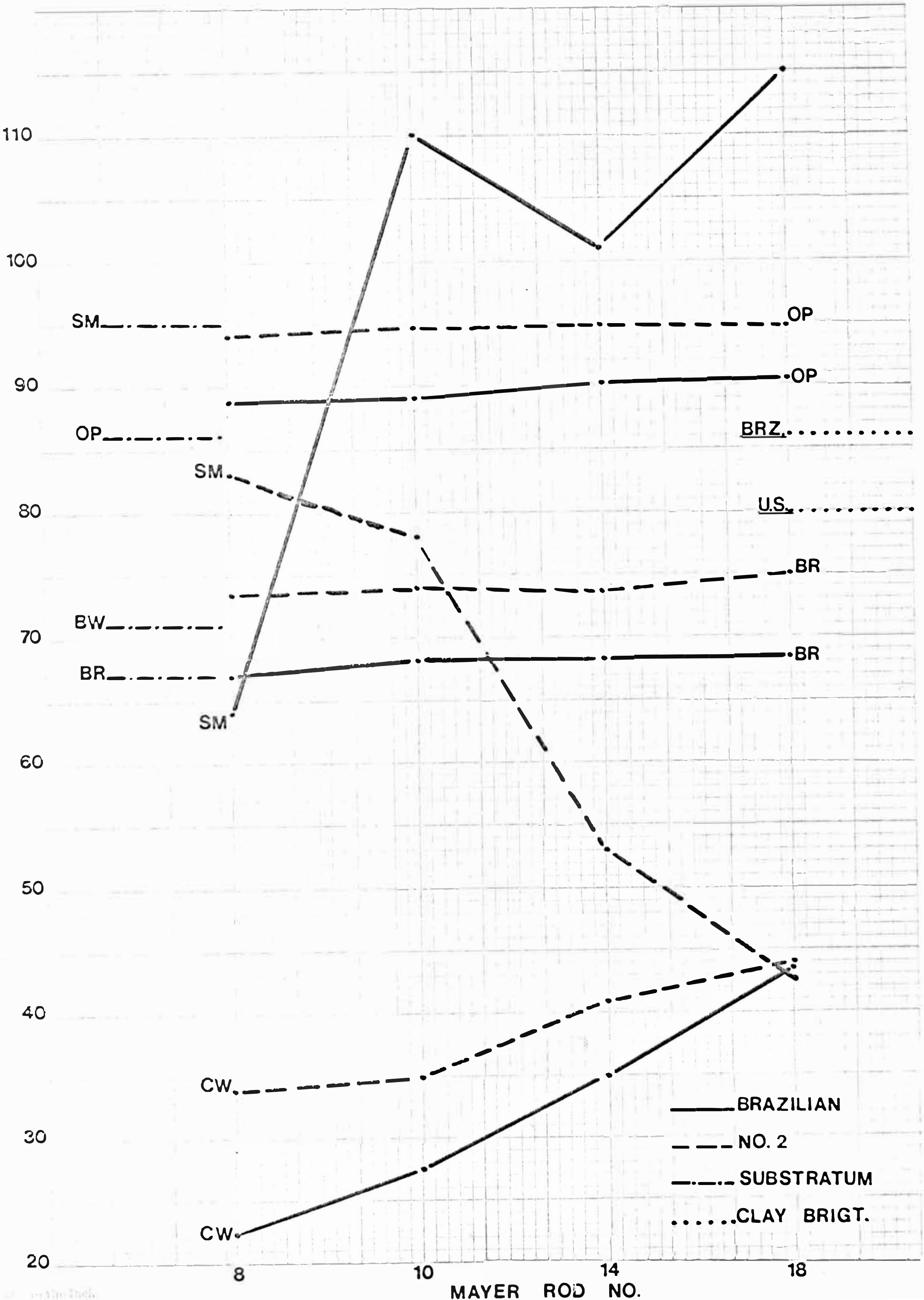
NO2 88 X LOW ANG. ILUM.

lowered the brightness results even further.

Sanches has reported loss of 7-8^{0} GE for Brazilian clays, and 2-3^{0} GE for Georgia Clays, when being applied. Comparitively, a loss of 17.5^{0} and 6^{0} GE respectively was measured in this work, possibly due to the low brightness of the substract.

Table of Physical and Optical Properties

Brightness					
Rod No.	8	10	14	18	Base Stock
Braz	67.0	68.3	68.3	68.4	67.
No. 2	73.6	73.9	73.8	74.9	
Opacity					
Braz	88.0	89.0	90.4	90.4	86.2
No. 2	94.3	94.7	94.9	94.6	
Smoothness					
Braz	65.	110.	101.	115.	95
No. 2	83.	78.	53.	42.	
Coat Weight (g/m^2)					
Braz	22.2	27.5	35.0	43.5	71.2
No. 2	34.3	35.0	41.0	44.0	


110
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SM
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BW
BR
SM
SM
CW
CW
OP
OP
BRZ.
U.S.
BR
BR
BRAZILIAN
NO. 2
SUBSTRATUM
CLAY BRIGT.
8
10
14
18
MAYER ROD NO.

The surface of the paper after being coated shows a quite large loss of smoothness. The only time we improved smoothness was with bar No. 8.

No relative test for abrasion was run but some pictures taken from the final product show very large crystals present and also some black crystals we assumed to be Quartz. It was possible to see, with the help of a microscope with 88 X magnification, using reflected and transmitted light, the light being shined through the large crystals. Photographs 1 through 5 are attempts to show the crystals.

The abrasion of the clay was detected when chromed surfaces were badly scratched after one stroke of approximately 10 cm against the paper surface.

CONCLUSIONS

The only benefit from applying this coating appeared at very low coat weights, in the range of pre-coats, but the viability of applying such an abrasive coating on any kind of equipment is not too large.

It is believed that the clay, as it is, can not be used for coatings. Better cleaning of the clay with removal of larger particles is imperative. With a better particle size distribution, brightness, opacity, smoothness and abrasion problems could be minimized.

Further studies on the mechanics of color loss after being applied to the surface should be pursued.

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