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The Influence of Clay Flocculation and Dispersion on the Covering Power of Clay Coating Colors

Donald G. Pryor
Western Michigan University

Donald G. Pryor

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HISTORICAL SURVEY

Introduction

A survey of the literature showed that considerable information has been published on the effects of dispersing agents on the viscosity of coating colors and clay slurries. There seemed to be little work done on the effect of the dispersing agent on any other of the properties of the coating.

Inasmuch as that dispersing agents decrease the average particle size of the clay particles, the effect of decreased particle size constituted the basis of the problem which this paper discusses. As particle size decreases the surface area of the clay particles increases proportionally. It was felt that this phenomenon could effect the covering power of the color.

The historical survey was directed at learning what was involved in dispersion and flocculation. A brief discription of what was found follows this introduction.

CLAY PARTICLE

Clay, used in a general sense, refers to a group of naturally occurring minerals composed of hydrous aluminum silicate consisting of very fine grained crystal fragments and showing plastic properties.(1) Kaolinite, used extensively in the paper industry in clay coatings and as fillers, is a hydrated aluminum silicate mineral of definite chemical composition.(2)

The kaolinite crystal is composed of silicon, aluminum, hydrogen, and oxygen in the ratio of 2:2:4:9 respectively. The crystal is built up of alternating layers of silica and alumina. Hydroxyl and oxygen valence linkages bonds the layers of silica and alumina together. (1)

Woodward & Lyons (3) claims that the kaolinite particles which are predominantly under two millimicrons in diameter consists of flat pseudo - hexagonal plates. Those which are predominantly over two millimicrons in diameter are cemented stacked aggregates of these fine single plates.

The clay or kaolinite particles as viewed by Asdell (1), fractures along two lines. He says the

hydroxyl to silicon valence linkages are secondary bonds. Therefore they form a "natural cleavage plane". Futhermore the article claims that the negative charges on the particle "cannot be accounted for on the basis of fracture along the basal cleavage plane" as no unsaturation occurs because no primary valence bonds are broken, only the secondary valence linkages. The unsaturation results from fractures in the vertical direction where primary valence bonds are broken.

Asdell (1) further believes that these unsaturated active areas existing of the edges of the crystals are the cause of hydroxyl ions being preferentially adsorbed on the surface of the crystals immediately adjacent to these active areas. The hydroxyls being hydrated, will carry waters of hydration along when adsorbed and form a tightly held water hull around the clay particles.

The two previous paragraphs lay the basis for the ion exchange mechanism. Further discussion of this will be found under the heading "Ion Exchange".

FLOCCULATION AND DISPERSION

Flocculation is the formation of a cluster of particles which can be broken by; (4)

1. Relatively weak mechanical forces.

2. Physical forces acting at the interface of of the colloidial particles and the suspending medium.

Aggregates differ from flocculates in that relatively strong mechanical forces are required to break up the cluster of particles in an aggregate.(5)

Characteristics of the mechanism of flocculation are given by Fischer (5) as;

1. The particles composing the flocculate were at one time seperately dispersed in the continuous phase,

2. the flocculate is formed by movement of the particles within the dispersion by convection, stirring, or other means, and

3. "adherence" of the particles occurs.

While flocculation is the formation of a cluster of particles, dispersion is the breaking of these

formations. The limits placed on flocculates does
not apply to dispersion. Dispersion is a colliodial
system in which the particles are geometrically
independent.

Particle movement plays an important role in
both flocculation and dispersion. For flocculation
to take place particle movement must be present.
The attractive forces between particles are usually
insignificant to cause much flocculating. (6) The
movement of particles caused by mixing or milling is
usually great enough to cause at least some breaking
of flocculates. The particle movement needed for
flocculation is slight. Undoubtably the Brownian
Movement of the particles assist in flocculation.

The mechanical disarrangement of the particles
results in unstability. By employing variations in the
physical forces acting at the interface of the sus-
pending medium and the particles a stable dispersion
can be prepared. Those variations in the forces at
the interfaces of the liquid and solid are the subject
on "Ion Exchange".

ION EXCHANGE

Very simply, ion exchange involves the exchanging of ions clustered around a colliodial particle. This exchanging of ions will influence the hydration capacity of the particles and the degree to which the particles exist in flocculates.

The discussion of the clay particle emphasized the importance of the hydroxyl ions which exist absorbed on the kaolinite crystal. Asdell(1) explains the existence of the water hull by the unsaturated valence bonds existing on the edges of the kaolinite crystal.

Kaolinite is known to be a hydrous material whose hydration capacity is subject to variations. According to Asdell(1) the negative adsorbed hydroxyl ions attract positive ions from the surrounding vehicle.

Grim (7) relates the property of certain clays to form in a sticky plastic mass to the variations in hydration according to the exchangable base (ion) present. If the adsorbed cation is of low hydration

6.

capacity there will be a thin water film around the particle and result in the particles clinging together and would form a sticky plastic mass. A thick water film resulting from a cation of relatively high hydration capacity resident on the kaolinite surface would yield a less sticky mass, but still showing plastic properties.(7)

This water hull is discribed in Hartman's "Colliod Chemistry"(8) as the "diffuse double layer". He considers the interlayer to be the adsorbed hydroxyl ions and the outer layer to be the cations. The interlayer of ions are fixed and concentrated, while the outer layer to be loosely held and to consist of both positive and negative ions. The greater concentration of charges of opposite sign than those of like sign are in close proximity to the surface of the particle. The concentration of each ion becomes closer to being equal as the distance from the charged surface is increased until they are equal.

As indicated in previous paragraphs the size of the water hull is the factor most important in determining

whether the colliodial system is flocculated or dis-
persed. Its importance is readily seen by consideration
of the formula (1);

$$Zeta = \frac{4\pi ed}{D}$$

Zeta can be considered as the repulsive forces
acting between the particles suspended in a liquid.
Zeta can be increased by increasing e, the adsorbed
electric charge or increasing d, the thickness of the
water hull, or by decreasing D, the dielectric constant
of the medium.

To increase the thickness of the water hull,
the hydrogen ions are replaced by ions having a higher
hydration capacity, such as sodium ions.

When this exchange reaction is complete there
will be a rise in p H because of an increase in
hydroxyl ion concentration causing more hydroxyl ions
to be adsorbed onto the particles and therefore causing
an increase in charge e. The sodium ions will cause
a large decrease in the dielectric constant D.

Another approach to the explaination of the
importance of the size of the water hull is consideration

of the attractive and repulsive forces and the distance
through which each can act effectively.

Van der Waals forces, the natural attraction of
mass for mass, are considered to be the forces of
attraction in a flocculated system. For these attract-
ive forces to take effect the particles must be within
three Ångstrom units.(9)

Now if these repulsive forces are allowed to
act the particles will not flocculate. When ions of
low hydration capacity collect around the particles,
a thin water hull results. A thin water hull shows
that the counter charges are relatively concentrated
around the clay particle and will neutralize the charges
on the particles within the three Ångstrom units which
attraction will take place. If the counter charges
are highly hydrated they will be less dense and will
not neutralize the negative charges within three
Ångstrom units, thus allowing repulsion to take place.

If an excess of highly hydrated cations are added
to a dispersed collidial system, by the law of mass

action more of these ions will be forced into the
water hull. The result of this will force these ions
to neutralize part of the preferentially adsorbed
hydroxyl ions.(1) The charge e is reduced and the
size of the water hull is also reduced. Both will cause
a reduction in the effectiveness of the repulsive
forces and can result in flocculation if the excess
is sufficient.(1)

EXPERIMENTAL WORK

Preliminary work done before actual investigation of the influence of clay flocculation and dispersion of the covering power of clay coating colors, was done on clay slurries.

Preparation clay slurries. Ten slurries were prepared with different percentages of tetra-sodium pyprophosphate (0.05%, 0.10%, 0.20%, 0.30%, 0.40%, 0.60%, 0.90%, 1.20%, 1.50% and 2.00%) based on the clay present. Stellar clay was added to a Hobart mixer and distilled water containing the tetra-sodium pyprophosphate was very gradually mixed in. All slurries contained approximately 60% clay by weight.

An attempt was made to examine these preparations in three ways:

1. viscosity differences
2. sedimentation rates
3. microscopic examination

Viscosity differences were visually noticeable and therefore didnot require the use of a viscometer

to determine if and how the viscosity changed.

The rate of sedimentation of the clay in slurries was done by diluting the 60% clay slurries to 1% and allowing to settle for one week in one liter flasks.

Microscopic examination, using 60 and 100 magnification, was done by placing a drop of the clay slurry adjacent to a drop of water on a glass slide. A cover glass was then placed on top of the slide.

When looking through the microscope, pressure was applied and then taken off the cover glass. The pressure caused the aggregates to break up. It was hoped that the degree of dispersion could be estimated by observing the particles after releasing the pressure.

Preparation of Coating colors. The experimental work consisted of preparing two clay slurries, one with 0.3% tetra-sodium pyrophosphate and the other without this dispersing agent. An adhesive was added to each slurry to form two coating colors, one with dispersed and one with flocculated clay. Using wire wound doctor rods and

12.

Bird applicators these coatings were applied to low
brightness base stock. All samples were dried at
room temperature (70 to 80° F). These coated samples
were then evaluated on a G. E. Brightness Tester.
The brightness results were plotted against the weight
of coating on the bare stock and the curves for the
two coatings were compared.

The coated samples prepared and evaluated can
be divided into two groups:

1. Those containing poly vinyl alcohol as the
sole adhesive.

2. Those containing starch as the sole adhesive.

Preparation of these coatings was the same as
in the preparation of the clay slurries with the add-
itional step of gradually adding the adhesive to the
slurries in the Hobart mixer.

The poly vinyl alcohol used was duPonts' "Elvanol",
high viscosity 72-51 poly vinyl alcohol. It was
prepared by adding very gradually the powdered
Elvanol to cold water which was being agitated by a
Hamilton Beach mixer. This was heated to 75° C with
constant mixing and then allowed to cool.

Stayco M starch solution was prepared by stirring the powder into cold water and heating to 90°C.

All coating colors were prepared at solid levels where the flocculated clay coating would have approximately the same viscosity as the dispersed clay coating. The dispersed clay coating was prepared at a desirable viscosity level and the flocculated was made to match it.

<u>Coated samples containing Elvanol.</u> Unbleached paperboard (70lb. per 1,000 sq. ft.) was used as the base stock for the draw downs prepared with R. D. Specialties rod No. 8. A 8 X 14 inch glass plate, raised 1/2 inch at one end, was used as a foundation. Three sets of samples were prepared:

1. Ten 6 X 12 samples of each color were prepared with from one to ten coats.

2. Seven 6 X 12 flocculated clay samples and seven 6 X 12 dispersed clay samples, all made with No. 8 rod and from one to seven coats applied to the samples.

3. Three 6 X 12 samples of each color were prepared with four, six and eight coats for the one, two and three samples respectively.

These were not calendered.

Coated samples containing starch. Unbleached
kraft wrapping paper (50 lb. 25 X 37 - 500) was
cut into 6 X 12 sheets and coated with R. D. Specialties
rods Nos. 3, 8, 12, 15, 18, 20, 24, and 30 and with
Bird applicators Nos. .005, .010, .015 and .030.
Duplicate samples were prepared with the Bird applicator.
Draw downs were made as before.

These samples were super calendered 2 nips
after air drying.

Evaluation

The G. E. Brightness tester, set on filter No. 1
was used to get all the data on the covering power
of the coatings at various coating weight levels.
Three different readings were averaged and reported
as the brightness of each sample.

Coating weight was determined by cutting uniform
portions from the large samples with the Taber
Stiffness sample cutter. These were weighed on the
analytical balance and the weight reported.

Table I

		Adhesive		Stellar	Clay
Elvanol	Dispersed	90 gram of	360 ml water	300 gram clay	500 ml water 0.9 gram tetra-sodium pyprophosphate
	Flocculated	60 gram of	40 grams Elvanol	200 gram clay	580 ml water
Starch	Dispersed	128 gram Stayco starch 640 ml water		640 grams clay 240 ml water 2.4 gram tetra-sodium pyprophosphate	
	Flocculated	128 gram Stayco starch 640 ml water		640 grams clay 240 ml water	

(Note: the "360 ml water" and "40 grams Elvanol" are bracketed together for the Elvanol section)

RESULTS

Preliminary Experimental Work

The changes observed in viscosity by increasing the amount of tetra-sodium pyprophosphate were noticeable. With 0.05% tetra-sodium pyprophosphate it was very difficult to make of 60% solids clay slurry and with 0.3% tetra-sodium pyprophosphate a minimum viscosity was obtained. A very gradual increase in viscosity occurred by increasing the per cent of tetra-sodium pyprophosphate and at 2.0%

tetra-sodium pyprophosphate the slurry was somewhat viscous but less than that with the 0.2% tetra-sodium pyprophosphate.

Sedimentation and microscopic procedures failed to give results consistent with known information.

Coated Samples Containing Elvanol

Table II

R.D. Speciality Rod No. 8

No. of Coats	G. E. Brightness		Coat Weight	
	Disp.	Flocc.	Disp.	Flocc.
1	62.5	62.8	.8423	.8546
2	75.9	72.6	.8601	.8032
3	78.9	74.2	.9104	.8894
4	79.8	79.2	.9404	.8937
5	80.0	80.1	.9583	.9491
6	80.0	80.6	.9520	.9264
7.	80.3	80.2	.9826	.9382
8	80.0	80.3	.9989	.9850
9	80.0	80.4	.9897	.9900
10	79.1	80.0	1.0608	.9826
1	63.0	63.4	.8468	.8501
2	74.8	72.0	.8737	.8501
3	77.6	76.5	.8876	.8756
4	79.0	78.6	.8923	.8793
5	80.5	80.4	.9108	.9047
6	79.8	80.6	.9067	.9220
7	80.3	80.3	.9454	.9306
4	78.0	78.1	.8906	.8661
6	79.5	80.6	.8998	.8592
8	80.6	79.8	.9519	.9311

The results obtained from the evaluation of clay flocculated and clay dispersed coatings, containing Elvanol are shown in Table II. Shown in Figure I are the curves of the brightness values of the flocculated and dispersed clay coatings versus this coating weights.

Due to the fact that there was a jump of nearly ten G.E. Brightness points where there were no sample brightnesses to plot, there leaves room to question the results as illustrated graphically.

To gain more information of the charactistics of flocculated and dispersed clay coatings, a second set of samples were prepared and evaluated. The changes were made in this second set of coated samples because,

1. Elvanol acts to some extent as a protective colliod and, therefore, may disperse the flocculated clay to some degree.

2. Elvanol does not contribute to the brightness of the clay, but causes some degree of transparency.

3. To compare previous results with results obtained from the second set of samples can be applied to the Elvanol coated sample results.

Coated Samples Containing Starch
Table III

Coat Application R.D. specialties rods	Brightness		Coat Weight	
	Disp.	Flocc.	Disp.	Flocc.
No. 3	63.8	55.2	.2425	.2328
No. 8	67.5	50.6	.2731	.2126
No. 12	66.1	58.2	.2616	.2385
No. 15	66.8	58.6	.2624	.2449
No. 18	67.8	59.0	.2689	.2408
No. 20	67.9	63.1	.2775	.2499
No. 24	69.5	65.7	.2958	.2541
No. 30	70.0	68.4	.2988	.2623
Bird Applicator				
No. .005	54.5	48.2	.2077	.1990
No. .005	56.4	49.1	.2122	.2031
No. .010	58.9	51.2	.2289	.2164
No. .010	60.5	53.5	.2269	.2208
No. .015	63.4	61.0	.2383	.2528
No. .015	64.2	68.8	.2420	.2418
No. .030	66.0	68.6	.2619	.2720
No. .030	67.3	70.3	.2805	.2833

The results obtained from the coatings containing starch as the adhesive are tabulated in Table III. When the flocculated clay coating and the dispersed clay coating results shown in Table III are plotted as were the results in Table II, a noticeable difference can be seen (Figure II).

The relationship between these two curves are:

1. At heavier coat weights, where nearly complete coverages exist, there is little difference in brightness, and the curves approach each other.

2. The curves seem to have a tendency to come together at the low coat weights where there is very little coverage.

3. As these coating colors were prepared at different solids levels and or the starches were prepared seperately, there is adequate room for some experimental discrepencies which is might account for the flocculated clay curve to cross the dispersed clay curve, at high coating weights and then to run parrellel with it.

4. The flocculated clay coating curve was drawn
so as to represent the scattered points obtained
when the results in Table III were plotted. This
indicated that the flocculated clay coating was
less stable and/or not as uniform as the dispersed
clay coating.

5. In the nearly vertical portion of the flocculated
clay coating curve brightness values increased almost
ten points without a significant increase in coat
weight, indicating that covering power develops
much more rapidly than it does with a dispersed
clay coating color once the flocculated color reacted
a critical value.

CONCLUSIONS

Literature advised the use of 0.3% tetra- sodium pyrophosphate based on the clay to obtain a minimum viscosity. Using Stellar clay and preparing a 60% solids clay slurry in a Hobart mixer a minimum viscosity point was reached by adding 0.3% tetra-sodium pyrophosphate. Both 0.2% and 0.4% tetra-sodium pyrophosphate slurries were more viscous.

The G.E. Brightness evaluated two independent groups of samples. A graphic representation of the results obtained were very similar. A significant difference in brightness of dispersed and flocculated clay coatings were seen at low coat weights. Flocculated clay coatings brightnesses fast approached the bright-nesses of dispersed clay coatings with minor coat weight increases. Flocculated clay coatings brightnesses were slightly higher than dispersed clay coatings brightnesses at high coat weights.

Figure I

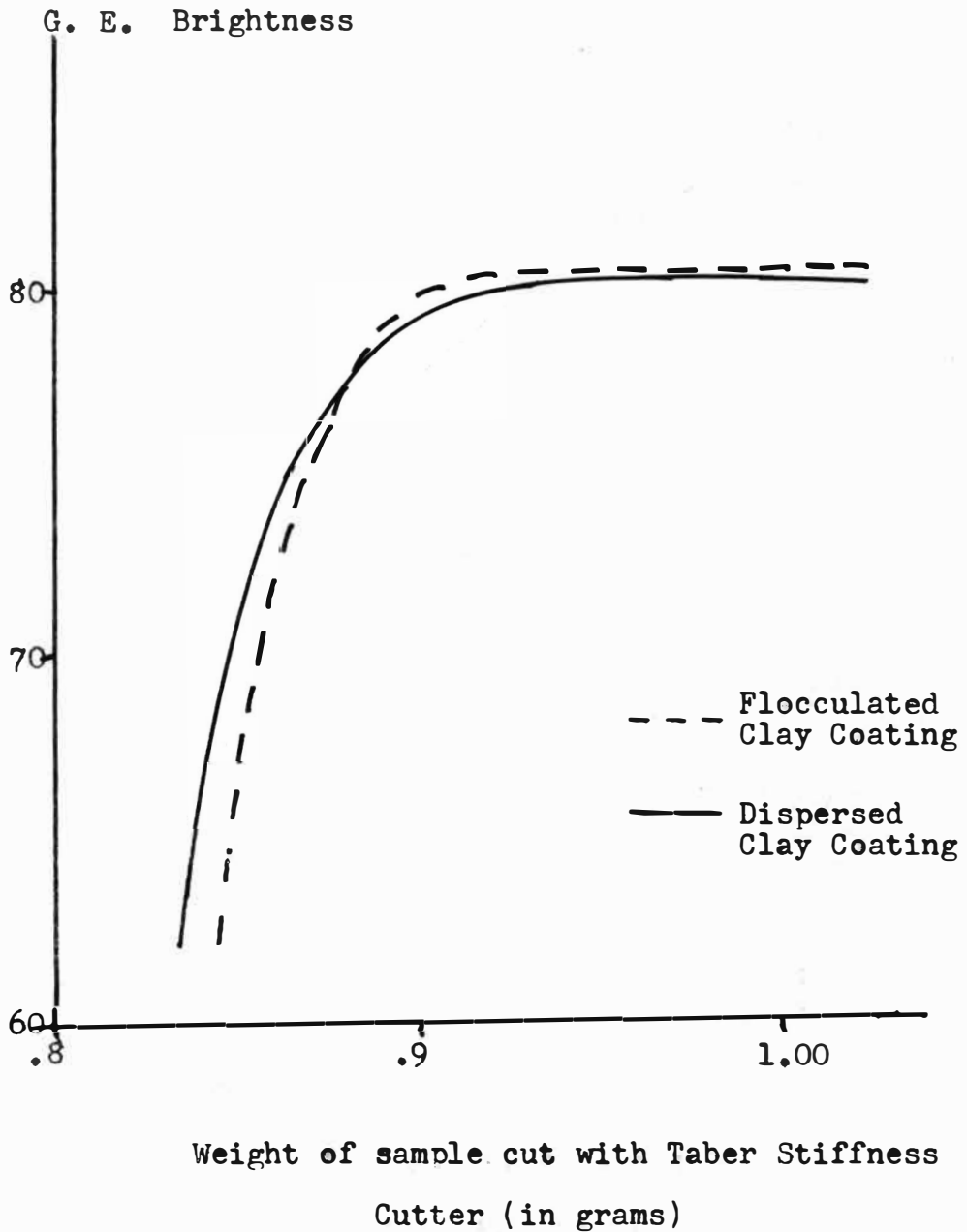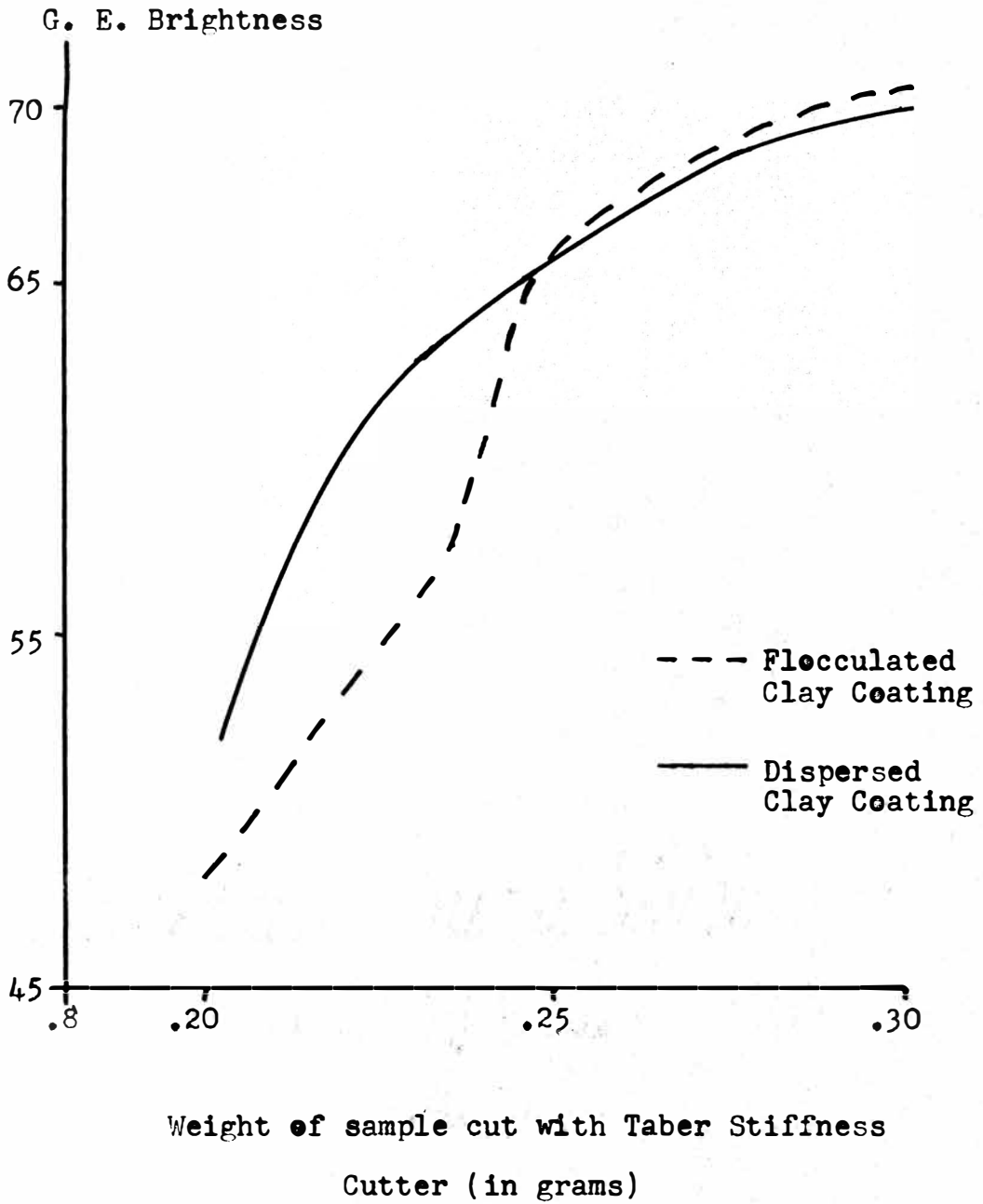Elvanol Coating Brightness vs Coat Weight

G. E. Brightness

- - - Flocculated
       Clay Coating

——— Dispersed
      Clay Coating

80

70

60

.8   .9   1.00

Weight of sample cut with Taber Stiffness

Cutter (in grams)

Figure 2

Starch Coating Brightness   vs   Coat Weight

G. E. Brightness

- - - Flocculated Clay Coating

——— Dispersed Clay Coating

Weight of sample cut with Taber Stiffness Cutter (in grams)

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