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Research Report

FLUSHING OF PIGMENTS

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TABLE OF CONTENTS

DUP030013834

INTRODUCTION

Most synthetic pigments at certain stage of manufacture exist as a water wet presscake. The transfer of presscakes directly from the aqueous into an organic phase is referred to as "flushing".

Flushing is an old art. Some of the early literature dates as far back as the late 1800's. The advantage of "flushing" have often been cited as (a) it avoids the aggregation of pigment particles taking place during the forced drying and the subsequent mechanical pulverization and (b) it gives dispersions of better quality. Flushed formulations revealed in early patents are mostly for specific vehicles such as cellulose esters, printing inks, etc. With the advent of new coating compositions, many are no longer applicable.

In F & F, a flushed dispersion of hydrous iron oxide pigment was used in the 1950's in Duco® lacquer. Its use has since declined with the advent of acrylic lacquers.

This report will describe our general studies of the flushing technology and specific applications in organosol lacquers. Also included will be the comparative costs of various dispersing processes and preliminary considerations of the role of flushing in mill base manufacture in terms of presscake characteristics, pigment types, cost and flushed base quality.

OBJECTIVES

The overall objective is to assess the role of flushing in F & F's dispersion manufacture.

The technical objectives for the reporting period have been to develop better understanding of general flushing technology and to demonstrate applicability of flushed dispersions of selected pigments in a specific product line, i.e., organosol lacquer.

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SUMMARY AND CONCLUSIONS

- A simple and economical flushing process has been developed. The process involves low shear mixing of a mixture of presscake/solvent/flushing agent/AB dispersant followed by a continuous centrifugation. The actual flushing is carried out at the mixing stage and the removal of residual water as well as coarse agglomerates accomplished simultaneously in the centrifugation step. The process should generally be applicable to presscakes that can be well deflocculated in organic medium and contain only moderate amount of agglomerates (0-40% depending primarily on the cost of the pigments).

  The processing cost was estimated to be $0.36-0.44/lb. of pigment vs. $0.65 for "47" process and $1.32 for two-roll milling.

- The "mixing/centrifugation" process was successfully demonstrated with transparent iron oxide type of pigments. The flushed dispersions, intended for use in the organosol vehicles gave organosol lacquers of good shelf stability. However, the ultimate dispersion quality of the lacquer and that of the final film depends on the fundamental particle size of the presscake. This conclusion stems from investigation of the following practical systems:

(a) Using a Hilton Davis transoxide yellow presscake (precursor to W682), which was found to have fundamental particles ranging from 0.05-0.20μ, we obtained a flushed dispersion that gave metallic lacquer films of nearly equivalent or slightly lighter side-tone than a two-roll milled control dispersion. Improvement of the flushed quality possibly exists if fresh presscakes are used. In view of the above findings, the potential quality

DUP030013886

improvement with fresher presscakes and the superior shelf stability, we have recommended the implementation of flushed transoxide yellow (W682) in the organosol lacquers.

(b) Using a fractionated hydrous iron oxide pigment--an experimental sample synthesized in the laboratory which had a particle size range of 0.01-0.05μ, we obtained a flushed dispersion of excellent quality. The said dispersion was very stable in the organosol lacquer and gave drawdown films of exceptional transparency and metallic panels of very good two-tone characteristics.

- For presscakes that form floccules in the organic media or contain excessive agglomerates (>40%), a flushing process which includes a grinding step will be needed. Preliminary studies indicated that a "mixing flushing" or "W & P Mixing" followed by "sand grinding" would be a feasible process.

  The "mixing flushing/sand grinding" procedure was demonstrated on a CPC (copper phthalocyanine) presscake (precursor to W765). The flushed dispersion was superior than a "47" process control dispersion in terms of transparency and cleanliness of the drawdown film. The comparative economics (for the W765 dispersions) are yet to be determined. The translation of improved quality into cost savings is highly specific to the pigments involved and has to be dealt with on individual basis.

- Studies of general flushing technology revealed:

(a) There is a positive correlation between pigment flushability and surface non-polarity. Presscakes with surface non-polarity significantly more than 70% can be flushed easily into the organic phase. And those significantly less would require flushing aids.

DUP030013887

(b) The selection of flushing aids can be guided by the surface potential (positive or negative) of the presscakes determined with a Zeta meter. Positive surface potential will require an anionic water insoluble flushing agent and vice versa.

(c) The significance of pigment particle size on transparency and two-tone characteristics of metallic finishes can be explained in terms of a theorectical scattering coefficient v.s. particle size curve. The curve shows that maximum scattering for iron oxide pigment occurs at ~0.15μ and substantial transparency for particles 0.04μ or less. Experimental results of our studies are in good agreement with the above predictions of Mie theory.

- Some considerations, based on available information, of the role of flushing as an alternative way of manufacture of mill bases are as follows:

(a) The "mixing/centrifugation" process can offer substantial cost saving and two-roll equivalent quality for pigments to which it is applicable. The key factor is the availability of appropirate presscakes (in terms of particle size and compatibility of additives).

(b) The "mixing (low shear or W & P) sand grinding" process can offer superior quality than "47" process (at equal amount of grinding). The merit of flushing will then depend on the practical significance of the improved quality and how much it can offset the additional mixing (i.e., flushing) cost.

ACTION TAKEN OR PROPOSED

- The status of flushed transoxide yellow (W682) dispersion has been summarized in a separate writing (I. C. Chu to T. A. Ashe, 9/3/71) with copies sent to all concerned and a recommendation has been made for preparing the flushed dispersion in semiwork quantity for further evaluation and implementation in the organosol lacquers.

DUP030013888

- Pigments Department will be contacted regarding the know-how for manufacture of F-113-D (hydrous iron oxide) which, we found, consisted of very fine fundamental particle sizes in sub-light scattering range but unsuitable for use in acrylic finishes due to incompatible additives.

- An added goal of our program is the implementation of flushing technology in the refinishes area.

PATENT STATUS

Based on limited prior art search, we believe that the "mixing/centrifugation" flushing process is unique and unusual in terms of simultaneous removal of agglomerates and residual water; no heat nor vacuum being used in the removal of residual water; pigment deflocculation, high fluidity and low density being required of the flushed dispersion.

A patent proposal will be made on the "mixing/centrifugation" flushing process.

PUBLICATION STATUS

Our studies on (a) pigment surface energies and their correlation with flushability and (b) HLB (hydrophile - lipophile balance) requirements for flushing effectiveness probably contain publishable results. Additional data and examples are desired in both cases. Publication will be contemplated at an appropriate time.

ACKNOWLEDGEMENTS

Acknowledgements are due to K. J. Brzozowski, H. Jakubauskas, L. R. Harper, S. Wu, V. Kasmer, J. G. King (Flint) , W. Ross (Pigments) and J. Jackson (Pigments) for their helpful discussions and contributions.

Much of the laboratory work was skillfully carried out by M. Clark.

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DISCUSSION

I. GENERAL STUDIES OF FLUSHING TECHNOLOGY

Most synthetic pigments are prepared by a precipitation procedure. The precipitated pigments are washed free of acids and other water soluble impurities by pressure filtration. The filter cakes (frequently referred to as presscakes) of various pigments still contain 40-80% residual water which has to be removed by other means. The most commonly employed method has been oven drying followed by mechanical pulverizing. The products thus obtained are in the form of a dry powder. The dry pigments normally exist in a highly aggregated state, and considerable amount of mechanical work will be required to break-up these aggregates and redisperse them in appropriate liquids and resins. For many pigments--particularly those with a "hard texture", it would be difficult to reduce them to the original degree of fineness (as found in the precipitated state) by mechanical grinding.

"Flushing" offers an alternative route to manufacture of pigment dispersions. In "flushing", the presscakes are transferred directly from aqueous into the organic liquids or resins. The incentives of "flushing" are (a) it circumvents the processing steps of "drying" and "pulverizing" and (b) since the pigment particles in the presscakes are in a less aggregated or loosely agglomerated state, it requires no grinding or less grinding to achieve the same result of particle size reduction.

A key factor in "flushing" is the relative wetability of the pigment particles by water and oil (i.e., organic liquids or resins). In order to affect "flushing", the pigment particle must be preferentially wetted by the oil phase and water must be effectively displaced from the pigment surface. This factor has been studied in terms of the polar and non-polar surface energies of the presscake.

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A. FLUSHIBILITY OF PRESSCAKES

(1) The total surface energy of solids can be resolved into two components--the polar and non-polar contributions. A procedure for estimating the magnitude of the polar and non-polar components for polymeric materials has been worked out by S. Wu. (Ref. 1). K. J. Brzozowski, (Ref. 2) applied the technique to determine the surface energies of pigments and found there was a good correlation between the pigment surface polarity and deflocculation by AB dispersant (H5581).

We employed the same technique to characterize the surface energies of presscakes. The procedure involves oven-drying the wet presscake, pulverizing the dried presscakes with mortar and pestle, making compressed pellet and measuring its contact angles with water and methylene iodide. From the contact angle data, the polar and non-polar contributions to the total surface energy can be computed with the aid of a computer program (Ref. 3).

Some of the experimental difficulties encountered during the contact angle studies are worth mentioning:

- Presscakes and pigments with a hard texture were difficult to compress into a coherent pellet. The resultant pellet was very brittle with little coherent strength. Leaving the pellet in the press longer and applying higher pressure did not seem to help the situation. It was found that screening out the coarse fractions and using only particles that could pass through a fine sieve (<200 mesh) would increase the coherent strength sufficiently so that an intact surface large enough for contact angle measurement might be obtained.

- For a Monastral® red (W816) pigment, the compressed pellets prepared a few weeks apart gave significantly different contact angles with H_2O and methylene iodide. The cause of this discrepancy has not yet been identified.

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- Duplicate (or triplicate) pellets made on the same date by standardized procedure usually gave consistent and reproducible contact angle results.

Taking the precautions as stated above the surface energies of various presscakes were determined. The results are summarized in Table I. The flushability of a given presscake into an organic phase (i.e., toluene) is related to the % surface nonpolarity of the presscake (with the except of W558 of which the contact angles with H_2O and methylene iodide were suspected to be misrepresented due to artifact introduced at the pellet preparation). Presscakes with surface nonpolarity greater than 70% will most likely be flushed into the organic phase spontaneously, while those with surface nonpolarity less than 60% will most likely remain in the water phase.

(2) In another series of experiments, we considered the flushability of presscakes by the thermodynamic argument. The free energy change (ΔG) accompanying the transfer of a pigment particle from aqueous into an organic phase is given by

$$\frac{\Delta G}{A} = \gamma_{so} - \gamma_{sw} \qquad (1)$$

Where A = Surface area of the particle.

γ_{so} = Interfacial tension between pigment surface and the organic liquid.

γ_{sw} = Interfacial tension between pigment surface and water.

The interfacial tension of a small particle with liquids is difficult to determine experimentally. We choose to use a harmonic-mean equation developed by S. Wu (Ref. 4) to calculate the interfacial tension from the surface tension properties of the individual phases (i.e., pigment surface and liquid).

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$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \qquad (2)$$

Where γ_{12} = Interfacial tension between phases 1 and 2.

γ_1 = Surface tension of phase 1

γ_2 = Surface tension of phase 2

Superscript d = Dispersion (or nonpolar) component of the surface tension

Superscript p = Polar component of the surface tension

Equation (2) has been shown (Ref. 4) to give better fit to experimental values than Foukes' equation (Ref. 5) for liquid/liquid and liquid/polymer systems where polar materials are involved.

In order to apply equation (2), we need to know the polar and nonpolar components of the surface tension of water, organic liquid, and the presscake. The surface tension data for water and most organic liquids are available in the open literature and those for the presscakes can be determined in a manner described in the previous section.

The flushability data for a variety of pigments are given in Table II. These results show:

- The calculated free energy changes predict reasonably well the flushability of various pigments. Such correlation also indicates that equation (2) and the contact angle/pigment pellet technique have useful application to the practical flushing problems.

- For some pigments (i.e., W393, W673, W839, W537 and W552), although there was clear evidence that "flushing" had taken place, noticeable amount of pigments still remained in water. Flushing efficiency was generally poor.

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- Optimum flushing efficiency was observed when the free energy change had a larger negative value (-28 to -45 evgs/cm^2).

- A good correlation existed between surface nonpolarity and pigment flushability. Optimum flushing efficiency was noticed when surface nonpolarity exceeds 85%.

B. SELECTION OF FLUSHING AIDS

1. SURFACE CHARGE OF PRESSCAKES

For presscakes that do not flush into the organic phase spontaneously or have a poor flushing efficiency, it would be necessary to use a flushing aid (or transfer agent). Flushing aids are materials that adsorb on the pigment surface and alter the surface characteristics so that flushing (or flushing efficiency) can be promoted.

Adsorption can be divided into two types--chemisorption or physical adsorption. Chemisorption is very specific to the species involved and will be more difficult to predict on a generalized basis. Examples are Oleate-rutile (TiO_2) and Oleate-haemotite (Fe_2O_3) system (Ref. 6). Physical adsorption is due to Van der Waals interaction, hydrogen bonding and electrostatic attraction. Many known flushing aids are surface active materials of anionic or cationic types. Their physical adsorption behavior can be predicted from the ionic type, and the hydrophilic and hydrophobic portions of the molecule.

We have found that presscakes which required flushing aids consisted of particles either positively or negatively charged and they generally responded to ionic transfer agents of the opposite type. The results are shown below:

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Presscake Tested	Surface Charge	Type of Flushing Aid Required
Transoxide yellow (EXP920-65)	Positive	Anionic (dialkyl phosphate)
Lab. synthesized hydrous iron oxide (567E-28A	Positive	Anionic
Monastral® Blue (BT-463P)	Negative	Cationic (Tri alkyl quaternary ammonium salt)
Monastral® Blue (BT413-P)	Negative	Cationic
Bon Red Dark (RT-695-P)	Negative	Cationic

The surface potential of transoxide yellow pigment (W682) varies with the pH value of the aqueous medium. A Zeta potential* v.s. pH plot is shown in Figure 1. The surface charge was found to change from positive to negative at ~pH=10.3. In order to further test the selection rule illustrated in the preceeding section, we brought the pH value of the transoxide yellow (W682) presscake to 10.5 where, in accordance with Figure 1, the surface charge should be reversed. As would be predicted, we found that under such circumstances, it required a cationic transfer agent to effect the flushing. These results also indicate that in the flushing systems (i.e., water/oil mixtures), the ionic attraction is a major factor for promoting adsorption onto the pigment surface.

*The Zeta potential of a solid particle is the surface charge on the plane which divides the rigidly adsorbed charge layer from the diffuse layer.

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2. HLB (HYDROPHILE - LIPOPHILE BALANCE) OF FLUSHING AIDS

While the Zeta potential (or the sign of the surface charge) of the presscakes at the conditions of flushing will guide us to select the proper ionic type for the transfer agent, we noticed an additional requirement. This has something to do with the hydrophile-lipophile balance (HLB) of the transfer agent. Water soluble surfactants were shown to be poor transfer agents (i.e., for flushing). The following results illustrate this point:

EFFECTIVENESS OF FLUSHING AGENTS FOR TRANSOXIDE YELLOW PRESSCAKE (W682) AT PH = 6.8

	Ionic Type	Water Soluble	Effective as Flushing Aid
Bis(2EH) hydrogen phosphate	Anionic	No	Yes
Stearic Acid	Anionic	No	Yes
Tri Octyl methyl ammonium chloride	Cationic	No	No
Alkanol® BG	Anionic	Yes	No
Compound 88	Anionic	Yes	No
Sodium Lauryl sulfate	Anionic	Yes	No

Transoxide yellow presscake (W682) at PH=6.8 is positively charged and has a Zeta potential of +44. It therefore requires an anionic flushing agent. As anticipated, the cationic material (tri octylmethyl ammonium chloride) failed to act as flushing agent. Among the various anionic materials tested, however, only those with water insolubility were effective flushing agents; water soluble agents had either poor efficiency or no flushing effect at all.

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HLB puts the water and oil loving properties of amphipathic molecules on a numerical scale. It may serve as a useful criterion for general selection of transfer agents and a basis for simplification of experimental observations. In the following experiment, the flushing efficiencies of a series of fatty acids for the transoxide yellow presscake were determined (The fatty acids are known (Ref. 7) to form chemisorption on iron oxide surface).

A range of HLB numbers was included in this study by varying the size of the hydropholic portion of the fatty acid molecules. The effect of HLB on flushing efficiency is illustrated below:

FLUSHING OF TRANSOXIDE YELLOW (W682) PRESSCAKE INTO TOLUENE USING FATTY ACIDS AS FLUSHING AGENT

Flushing Agent	HLB*1	Flushing Efficiency*2
Propionic acid	7.7	1
n-Valeric acid	6.7	2
n-Caprylic acid	5.3	4
Decanoic acid	4.4	5
Lauric acid	3.4	4 - 5
Stearic acid	1.5	4 - 5

*1 - HLB values were computed by the Davies' equation (Ref. 8).
HLB = (hydrophilic group number) - n(CH_2 group number) + 7
-COOH (Group number) = 2.1
-CH_2 (Group number) = 0.475

*2 - Flushing efficiency was rated by the amount of residual pigment in the water phase
1 ——————> 5; No flushing ——————> complete transfer.

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The flushing efficiency is seen to increase with the size of the hydrophobic portion of the fatty acids up to 10 and 12 carbon atoms and begin to level off thereon. HLB values for optimum flushing efficiency appear to be in the range of 1.5 to 5.3. In comparison, the optimum range of HLB values is 3.5-6.0 for water/oil emulsification; 7.0-9.0 for wetting; 13.0-15.0 for detergent uses and 15.0-18.0 for colloid stabilization.

Other implications from the HLB/flushing efficiency studies are:

- Stearic and lauric acids are slightly less effective than decanoic acid. This indicates that the hydrophile and lipophile balance rather than the size of the hydrophobic portion is the dominating factor. Along this line of reasoning, we found that succinic acid end--capped AB dispersant (H5581) did not function as a transfer agent. Presumably the 5000 MW acrylic B-segment of H5581 outweighed the succinic acid A segment and the resultant HLB value for H5581 was lower than the optimum range (1.5-5.3).

- HLB values for ionic surfactants are not well documented because of the dependence of degree of ionization on environment. But the ionizable groups are generally assigned with very high hydrophilic values. A few examples from the published data (Ref. 7) are:

Ionic Group	Hydrophilic Number
$-SO_4\ Na^+$	38.7
$-COO\ Na^+$	19.1

It is seen that one sodium sulfate group can balance out the hydrophobic contribution from C_{80} hydrocarbon chain (MW $\tilde{=}$ 1100). It is therefore feasible that low molecular weight dispersant of the A-B type can be tailored to function also as a flushing aid.

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A single experiment was conducted to test the above idea. An A-B dispersant (5000 MW) having a quaternary ammonium A group (546E-136) was prepared through the courtesy of L. Harper. We found dispersant 546E-136 functioned effectively as a flushing agent. (Similar result would be anticipated if the succinic acid capped dispersant H5581 is neutralized). Unfortunately, the dispersant efficiency of 546E-136 was inadequate. It did not serve the dual function.

More study will be needed to determine whether this problem can be circumvented and a new series of molecules with a unique combination of properties can be created.

C. AGGLOMERATES AND FUNDAMENTAL PARTICLE SIZE IN PRESSCAKES

1. AGGLOMERATES

The degree of agglomeration and ease of breaking up varied from presscake to presscake.

Monastral® blue (BT463P) and green (GT-751-P) presscakes contained agglomerates that required moderate mechanical shear (such as Cowles Dissolver and W & P mixer with high viscosity conditions) to break them up. Optical micrographics of presscake BT-636-P (W552) subject to various mixing procedures are shown in Figure 2. Agitation in a simple propeller type mixing container obviously did not generate enough shear to effectively break up the agglomerates. This type of information must be on hand in order to select the appropriate process and equipment for flushing.

On the other hand, an auric brown transparent iron oxide presscake (F-113-P) was flushed over into the organic phase (toluene) with minimum mechanical shear and gave a dispersion containing little agglomerates. More discussions about this presscake (F-113-P) will be found in a later section.

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2. FUNDAMENTAL PARTICLE SIZE

The fundamental particle size was shown to have a prevailing effect on film transparency and two-tone characteristics apart from the overall pigment flocculation appearance in the final film. The details of this effect in relation to various pigments, lacquers and drawdowns will be discussed in their respective sections.

II. FLUSHED DISPERSIONS FOR ORGANOSOL LACQUERS

A. FLUSHED TRANSPARENT IRON OXIDES

A survey conducted in the initial phase of our work (Ref. 8) revealed that considerable interest existed in obtaining an alternative method for making transparent iron oxide dispersions. Current transoxide dispersions are either made by the costly two-roll milling process or purchased from outside dispersion houses at a premium price. Furthermore, these dispersions are often found unstable in the vehicles and lead to gellation and flocculation problems.

In view of the stated needs, we devoted a significant portion of our work to the flushing technology of the transparent iron oxide type of pigments. Our studies will be discussed in detail in the following sections.

1. TRANSPARENT IRON OXIDE YELLOW (W682)

(a) CHARACTERIZATION OF PRESSCAKE

The presscake (Code EXP. 920-65), which was a precursor for W682, was obtained from Hilton-Davis. As received, the presscake contained 62-67% water. The presscake was further characterized in terms of various properties shown in the following table.

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CHARACTERIZATION OF PRESSCAKE
(TRANSOXIDE YELLOW - W682)

Fundamental Particle Size	0.05-0.2μ
Agglomerates (or coarse fraction)	10-20% (on wt. of dry pigment)
Surface Charge (at PH=6.8)	Positive
Zeta Potential (at PH=6.8)	+44 MV
Flushability	Would not flush into organic media spontaneously
Flushing Agent Required	H_2O - insoluble amionic type (Bis(2-ethyl hexyl hydrogen phosphate)

The fundamental particle size was determined by electron microscopy (Figure 3). Particles in the 0.05-0.2μ range caused significant light scattering. This was evidenced by the slight haze of the wet dispersion and its milky appearance when viewed from a low angle.

The agglomerates (or coarse fractions) in the presscake could not be effectively broken up by a low shear propeller type of mixing. But they could be separated from the fine fractions by centrifugation (i.e., clinical centrifuge commonly used in the laboratory). These agglomerates, if present, would significantly degrade the dispersion quality. Therefore, they must either be de-agglomerated or be removed from the flushed dispersion.

Surface charge, Zeta potential and the flushability of the presscake have been discussed in Part I. Bis(2-ethyl hexyl) hydrogen phosphate was selected as the working flushing agent because it had excellent flushing efficiency and insignificant effect on the organosol film appearance.

(b) PROCESS CONSIDERATION

Conventional flushing is usually carried out in a heavy duty mixer (such as W & P mixer) where the presscake

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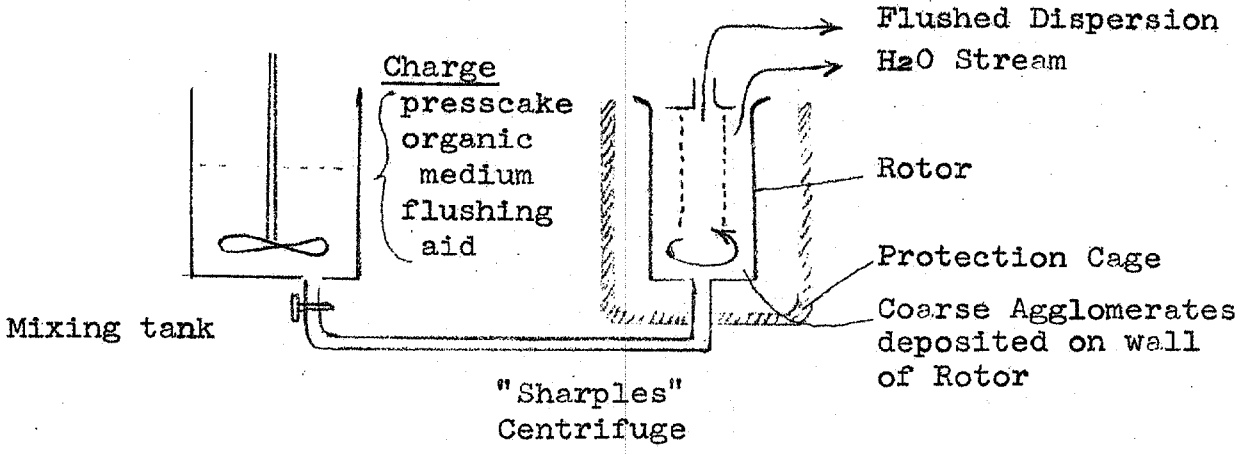
and the polymeric resin form the highly viscous mass. The aqueous phase separated from the viscous mass is mechanically decanted followed by vacuum distillation or sheeting on a two-roll mill to remove the trapped residual water. The thick mass resulted from the above operation requires additional mixing or grinding to reduce its consistency to a manageable level. The process is costly because of the multi-step operation and not suitable for handling the fluid A-B dispersions used in the organosol lacquers.

The "FB" (flushed base) flushing process at Parlin Plant is simpler and more economical. The equipment consists of a large mixing tank (type used for "49" process) equipped with propeller type agitators, heat jacket, vacuum, condenser and water trap. Flushing is carried out in the mixing tank under fluid and low shear conditions. When flushing is completed, the mixture is let stand until the water separates into a distinct phase which is then removed by siphoning. The residual H_2O trapped in the organic phase has to be distilled off. Since the process consists of no high shear operation, a major pre-requisite for applying this process is that the presscake must be reasonably free of agglomerates and unacceptable coarse size fractions. (The presscakes (F-4P) used in the Parlin flushed hydrous iron oxide dispersion for the Duco® products was provided fresh by Pigments Department. F-4P has since been discontinued due to sub-standard particle size and shape required by the current glamorous finishes). The transoxide yellow (W682) presscake, as shown by the characterization studies, contains significant amount of agglomerates and, therefore, can not be used directly in the "FB" process without introducing additional size reduction operations. The "FB" process, however, has the merit of simplicity and economy, it will receive due consideration whenever it is applicable.

The flushing process developed for transoxide yellow (W682) presscake is illustrated in the following schematic diagram.



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In the laboratory, the flushing was carried out in a wide mouth jar with an air drive stirrer. Presscake, water, solvent (toluene) and transfer agent (Bis (2-EH) hydrogen phosphate) were charged into the container in proper amounts. The mixture was subject to mild agitation with an air stirrer for 20-30 minutes. By then,the aqueous phase should be well separated from the organic/pigment phase and decanted manually. Following the decantation of the bulk water; an A-B dispersant (H5581) was added to deflocculate and stabilize the flushed-over pigment particles. The flushed dispersion of transoxide yellow was then centrifuged in a standard clinical centrifuge (A.H. Thomas Co) designed for laboratory use. Residual H_2O and coarse agglomerates were simultaneously removed and a fluid and stable dispersion of W682 was obtained. A typical formulation of the flushed W682 dispersion is given in Table III.

The laboratory procedure was further demonstrated with a continuous centrifuge ("Sharples" model) as shown in the sketch. The mixture from the mixing tank was gravitation-fed into the "Sharples" centrifuge which rotated at a pre-set speed. Two streams of liquids came out of the centrifuge continously--one was primarily water, and another the flushed dispersion.

The advantages of the "mixing/centrifugation" flushing process are:

- It is simple and economical (see next section)
- It removes residual water and coarse agglomerates in a single efficient operation. It thus elliminates the need of vacuum distillation and grinding.
- In comparison to the "FB" process, there won't be any foaming problem which could occur during the vacuum distillation (in the "FB" process).
- Potentially it can fractionate the particle size and therefore regulate the dispersion quality.

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The requirements for applying the "mixing/centrifugation" flushing technology are:

- The majority of pigment particles must be small and deflocculated.
- The dispersion should be reasonably fluid.

C. ECONOMICS

A preliminary study of the manufacturing costs of "FB and "mixing/centrifugation" flushing processes was made by J. P. Herring, Engineering Department, at my request. The results were summarized in a letter (I. C. Chue to F. N. Jones, April 21, 1971; see Appendix I).

For comparison, the mill base manufacturing costs by the various existing processes are included in the following table.

MILL BASE MANUFACTURING COSTS BY VARIOUS PROCESSES

Process	Cost ($/lb. of Pigment Processed)
*(1) "47" Process	0.65
At 12% Pigment Cone	
*(2) Two-Roll Mill	1.32
(a) W & P Cost	(0.40)
(b) Two-Roll Milling Cost	(0.55)
(c) "49" Process	(0.37)
*(3) "FB" Flushing Process	0.52
At 23% Pigment	
(4) "Mixing/Centrifugation" Flushing Process	0.36-0.44

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MILL BASE MANUFACTURING COSTS
BY VARIOUS PROCESSES (CONT'D.)

Process	Cost ($/lb. of Pigment Processed)
*(5) Conventional Flushing Process	0.77
(a) W & P Cost (at 30% Pigment)	(0.40)
(b) "49" Process	(0.37)

It is to be noted that the divisional figures were averaged over all mill bases (prepared by the same process; for example "47" process) that went into various end products. The actual cost for manufacturing a particular high quality dispersion from a given pigment can be significantly higher than the average figure depending on the pigment concentration in the mill base and the number of passes through the mill etc. Recognizing the possible variation from individual to individual cases, we can still obtain an overall picture of the cost associated with each process. It is seen that the flushing processes (Cases 3, 4 & 5) on the average compare favorably against the conventional processes (Cases 1 & 2). Among the flushing processes, the "mixing/centrifugation" process has an estimated economical edge over the other two.

In our opinion, there should also be some cost savings at the pigment manufacture end. However, Pigments Department indicated that the cost of presscake (on dry basis) would be essentially the same to the dry bagged pigment (Ref. 9). This means that the economics of "flushing" will be justified solely on savings of the cost of mill base manufacturing and/or technical advantages. We will be reviewing our program closely in light of these two factors (see later sections).

*Divisional average cost figures (as of 1970) compiled by E. T. Brewer.

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D. EVALUATION (V.S. Two-Roll Milled Control)

A mill base is an intermediate product. Its usefulness has to be judged in terms of its stability in the end products (i.e., paints) and its performance in the final films as well as those of the mill base itself. An in-depth evaluation of the flushed transoxide yellow) (W682) dispersion (Coded 538E-115) was conducted in comparison to a two-roll milled control.

The results are given in Table IV from which the following summary regarding the implementation of flushed transoxides in the organosol lacquers may be made.

> The flushed W682 dispersion (538E-115) contained coarser particle size (0.05-0.20μ). The dispersion quality of the flushed mill base was therefore not as good as the two-roll milled control (in terms of transparency and cleanliness appearance). However, the flushed dispersion showed better stability in the organosol lacquers than the two-roll milled control. In the final films, both dispersions were flocculated: in the solid color films, the flushed dispersion flocculated to a much lesser degree; in the metallic films, the degrees of flocculation, as exhibited by the electronmicrographies (Figures 5A and 5B), were equivalent but the two-roll milled control gave slightly better two-tone characteristics. The organosol lacquer prepared from two-roll milled W682 (912-G-60886) dispersion showed aging effect, while that from the flushed dispersion (538E-115) was stable over the same aging period (1 week).
>
> For glamorous metallic finishes, a strong side tone is a major quality-determining factor. In this regard, the organosol

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lacquer based on the flushed dispersion (i.e., W682) is nearly equivalent to that of the two-roll milled control. This--in combination with lower manufacturing cost (estimated in the previous section), better stability in lacquers and quality improvement potentially achievable with the use of fresher presscakes--has led us to urge that the flushed transoxide yellow dispersion be seriously considered for implementation in the organosol lacquer (Ref. 10).

Other findings and implications worth discussing from Table IV include:

- The dispersion quality in the final film stage is far inferior to that of the mill base. This applies to both the flushed dispersion and the two-roll milled control--the later being deteriorated to a greater degree.

  Close examination of the flocculation pattern in the final film (Figures 4A and 4B) reveals that it resembles very much the phase structure of the organosol film--the discrete phase being smaller near the surface and growing larger near the bottom. The pigment particles obviously are preferentially associated with the discrete phase and take on a flocculation pattern similar to that of the phase structure. The sizes of the discrete phase in the film derived from the two-roll milled control dispersion (Fig. 4A) are significantly larger than those from the flushed dispersion. Since the two panels were prepared under otherwise identical conditions, we deduced that the large phase structure was caused by factors existing in the two-roll milled dispersion but absent in the flushed dispersion. At least two factors appeared to have some bearing on this problem (a) the dispersant (RCH-14639) molecular weight in the two-roll

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milled dispersion was shown by GPC to be significantly lower (~ one half) than the molecular weight of the original dispersant and (b) the additives present in the pigment. Molecular weight decrease is inherent in the two-roll milling process; whereas contamination inherited from the pigment. The flushed dispersion avoided the former factor but not the latter and consequently an improvement in degree of deflocculation quality was observed. In another experiment (Section II A(2)), the fine fraction of laboratory synthesized hydrous iron oxide pigment was used to avoid additives in the commercial pigment and a film of exceptional transparency was obtained.

Of course, the sizes of the discrete phase in an organosol film can also be influenced by formulation and application conditions. And in this regard, it may indirectly alleviate the dispersion problem in films in-so-far as the flocculation is phase-structure associated. But the basic solution in our opinion lies in the removal of adverse causes in the mill bases, as this would decrease the complexity of paint formulation and broaden the formulation latitude.

- We would like to elucidate the effect of fundamental particle size on film appearance apart from the effect of pigment flocculation. This attempt has never been made in the past in our interpretation of film appearance and its relationship to pigment distribution because the two are closely related and difficult to separate.

  Work on the iron oxide pigment distribution in organosol films stimulated our thinking as to the individual contributions of the fundamental particle size and pigment floccules to the overall film appearance. Electron photomicrographics shown in Figures 5A, 5B and 5C are the cross sections of metallic organosol films pigmented with a two-roll milled dispersion (Fig. 5A), a flushed dispersion (538E-115) from a commercial presscake (Fig. 5B) and a flushed dispersion of the fine size fraction of a laboratory synthesized iron oxide pigment (Fig. 5C). The fundamental particle sizes of the three dispersions range in the following order:

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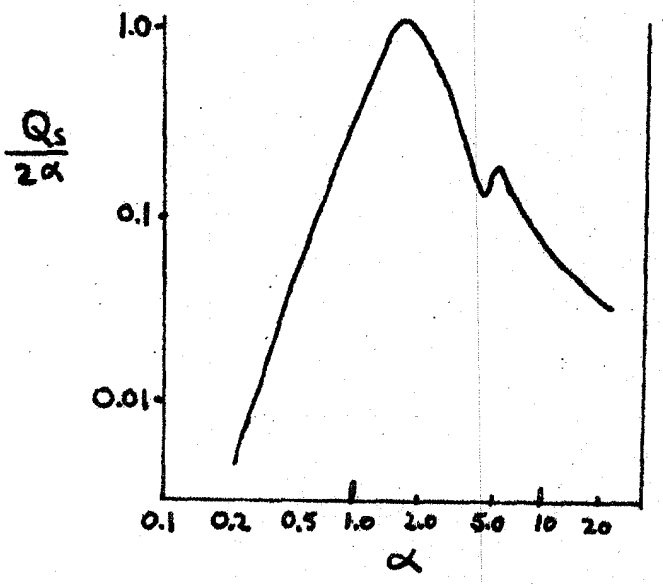
Flushed dispersion--commercial presscakes (~0.05-0.20μ) two-roll milled dispersion (~0.01-0.05μ) > flushed dispersion - lab. synthesized pigment (0.01-0.02 or less) the darkness of the side tone (i.e., the glamorous effect) of the metallic films arrange in exactly the reverse order. On the other hand, the pigment distributions (or the average size of the floccules) in the three films (judged by the electro photomicrographics) failed to show any correlatable trend--Figure 5A & 5B being equivalent and Figure 5C somewhat worse. This indicates that the fundamental particle size has an independent contribution to the film appearance apart from the pigment flocculation--particularly to the two-tone characteristics. As long as the degree of flocculation is moderate as in the cases represented by Figures 5 (A, B, & C), the fundamental particle size has a dominant effect on the two-tone characteristics which is believed to result from better transparency.

The following is a plot of light scattering coefficient as function of particle size for iron oxide pigment constructed from published data (Ref. 11).

FIGURE 11



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Where Qs = Relative effective cross section (of particle) for total scattering.

$$\gamma = \frac{\pi D}{\lambda'} \quad ; \quad \lambda' = \lambda / Nb$$

D = Diameter of Particle

λ' = Wave length of light in the binder in which the particle is imbedded

λ = Wave length of light

Nb = Refractive index of the binder

If we assume some reasonable values for λ and Nb say $\lambda = 0.471\mu$ and Nb = 1.5, then γ will be equal to 10D (λ = 10D). This will enable us to relate the scattering coefficient directly to the particle size. It is seen that the maximum scattering for iron oxide pigment occurs between 0.15 to 0.20μ (10-4 cm) and only particles in the size range of 0.01μ - 0.04μ have negligible scattering.

The results of our fundamental particle size studies are in good agreement with that anticipated from the theorectical treatment. And it explains why the fundamental particle size is a dominant factor for film transparency and two-tone characteristics.

The above conclusion points to a new direction for pigment dispersion research and new opportunities in the field of glamorous finishes through control and regulation of pigment fundamental particle size in combination with the dispersant technology.

2. SYNTHESIZED HYDROUS IRON OXIDE PIGMENT

The color of hydrous iron oxide presscakes has been known to change with time (Ref. 12). This is attributed to the growth of particle size in the water wet state. After the pigments are properly dispersed in the organic phase, the color will be more stable. To avoid color change and particle growth, it is therefore desirable to flush fresh presscakes.

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Attempts were made to synthesize hydrous iron oxide pigments in the laboratory, and flush them over into the organic phase from freshly precipitated filter cakes. We repeated the art of hydrous iron oxide syntheses revealed in three U. S. patents:

- U.S. 2,335,760, E. I. du Pont de Nemours & Co., 7/31/1941
- U.S. 3,398,113, Chemetron Company, 8/20/1968
- U.S. 3,565,656, Allied Chem. Company, 2/23/1971

The synthesized hydrous iron oxide pigments in all three cases showed broad range of size distribution and much coarser than what were claimed in the respective patents. Upon fractionation by centrifugation, the products based on U.S. 3,398,113 and U.S. 3,565,656 gave approximately 5-10% fines (estimated); and the product based on U.S. 2,335,760 contained only negligible amount of fines.

The following are the results of our evaluation of the synthesized hydrous iron oxide pigment, 567E-28 & 34 (U.S. 3,398,113).

- Pigment surface carries a positive charge and a Zeta potential of ~25 MV.

- The flushing aid (Bis (2EH)hydrogen phosphate) and flushing process ("mixing/centrifugation" procedure) employed for the transoxide yellow presscake (precursor to W682) are also applicable to the laboratory synthesized pigment (567E-28 and -34).

- The flushed dispersion derived from the fine fraction of 567E-34 exhibited a high degree of transparency and cleanliness without the milkiness appearance which was shown to be characteristic of the presence of high scattering particles. Figure 9 is an electron photomicrograph of Sample 567E-34. The loose fluffy agglomerates were formed during sample preparation where a drop of the diluted dispersion was laid on the carbon grit and dried. The single particles which formed the agglomerates were easily distinguishable and estimated to be 0.02μ or less.

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- The flushed dispersion is stable in the organosol lacquer. A single pigment tinting lacquer formulated from 567E-34 gave drawdowns (567E-31-3) of exceptional transparency. Electron photomicrographics of the cross section of the film (567E-31-3) are shown in Figures 10A and 10B. Again, as shown in the earlier films (Figs. 4A and 4B), the pigmented region was smaller near the surface and grew larger towards the bottom. As already discussed in previous sections, this pattern resembles the phase structure of the organosol film and the pigment particles are associated with the discrete phase regions.

- The metallic organosol lacquer derived from 567E-34 has already been discussed earlier. The superior two-tone characteristics (Figure 12) is attributed to the sub-scattering fundamental particle size.

The above work furnishes a lead to relatively trouble-free iron oxide dispersions and superior glamorous (metallic) finishes provided that we have access to presscakes of sub-scattering particle sizes or the know-how to make them effectively. Such a possibility may come from Pigments Department's know-how on F-113-D--an auric brown transparent iron oxide pigment. (See next section).

3. AURIC BROWN TRANSPARENT IRON OXIDE (W-461)

We have evaluated the presscake (F-113-P) for this pigment and found that it contained particles primarily in the sub-scattering region. The presscake could easily be flushed over into the organic phase (i.e., toluene) by the procedure described earlier and gave a dispersion of excellent appearance (i.e., transparency and cleanliness). An electron photomicrograph for the flushed dispersion is shown in Figure 13. Disregarding the few coarser particles which form the foreground, the majority of the pigment particles forming the background of this electron photomicrograph are in the sub-scattering region barely resolvable at 38000X magnification.

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The major drawback of F-113-D is that it cannot be used in acrylic vehicles. We have mixed the dispersion with (a) organosol, (b) current acrylic lacquer (RC-909), (c) acrylic refinish lacquer (RC-3176), and (d) Centari® refinish enamel (RC-3346). All gave poor results. The incompatibility of F-113-D with the agove vehicle lines is believed to be due to either the petroleum sulfonates or the amine compounds or both which have been added to the pigment during its manufacture (Ref. 13). However, if we could intercept the pigment at the precipitated state before the incompatible additives were introduced and applied materials compatible with the vehicle lines for which it is intended, this could provide a useful flushed dispersion with superb particle sizes for high quality finishes. We intend to touch base with pigments and pursue further along this line.

B. FLUSHED ORGANIC PIGMENTS - Monastral® Blue & Green

1. GENERAL CHARACTERIZATION

The flushing and dispersion problems of organic pigments are quite different from those of iron oxides. Some of the common characteristics of Monastral® (copper phthalocyanine) blue and green presscakes are described below:

- Fundamental Particle Size - The fundamental particle sizes of a Monastral® blue (W550) and green (W765) were determined by electron microscopy. W765 ranges primarily from 0.05 to 0.10μ (Figure 14); W550 has slightly smaller particles mostly in the range of 0.03-0.08μ (Figure 15).

- Flushability - Both W550 and W765 can be flushed into organic media without the use of any flushing aid. This would be true for many other organic presscakes as the pigments are basically organophilic. Some organic pigments (such as W552 and W537), however, have been surface treated to improve their dispersibility. Such pigments usually have insufficient flushability and flushing aids would be required for effective flushing. Suitable flushing aids are water-insoluble cationic surfactants such as tri octylmethyl ammonium halides.

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- Agglomerates - Are present in the presscakes of most of the organic pigments tested. For example, W552 (BT-463P) contains about 15-20% agglomerates. These agglomerates would not be broken up in a low shear flushing operation. Vigorous agitation or mechanical grinding would be needed to reduce the agglomeration.

2. CONSIDERATION OF FLUSHING PROCESS

The "mixing/centrifugation" process developed for flushing of transparent iron oxides unsuitable for some of the organic pigments on account of the following:

- Many organic pigments (i.e., W765, W550, etc.) exist in the organic media (solvents or resins) in a somewhat flocculated state. As indicated earlier (Section II A(1) - (b), pigment flocculation and non-fluidity interferes with centrifugal separation. Effective centrifugal separation would require that:

  (a) Pigment particles well deflocculated
  (b) Dispersion fluidity less than 50 cp (estimated)
  (c) Dispersion density less than water (i.e., 1.0 cp)

- Organic pigments are quite expensive (ranging from $4-$12/lb. in contrast to ~$1/lb. for the iron oxides). The agglomerates should be processed (i.e., deagglomerated) and fully utilized rather than removed (or discarded). A maximum of 5% pigment loss in the form of agglomerates during centrifugation may be tolerated without jeopardizing the economics of the centrifugation process. Other wise it would become economically unattractive, (unless the removed agglomerates can find uses in other grinding processes).

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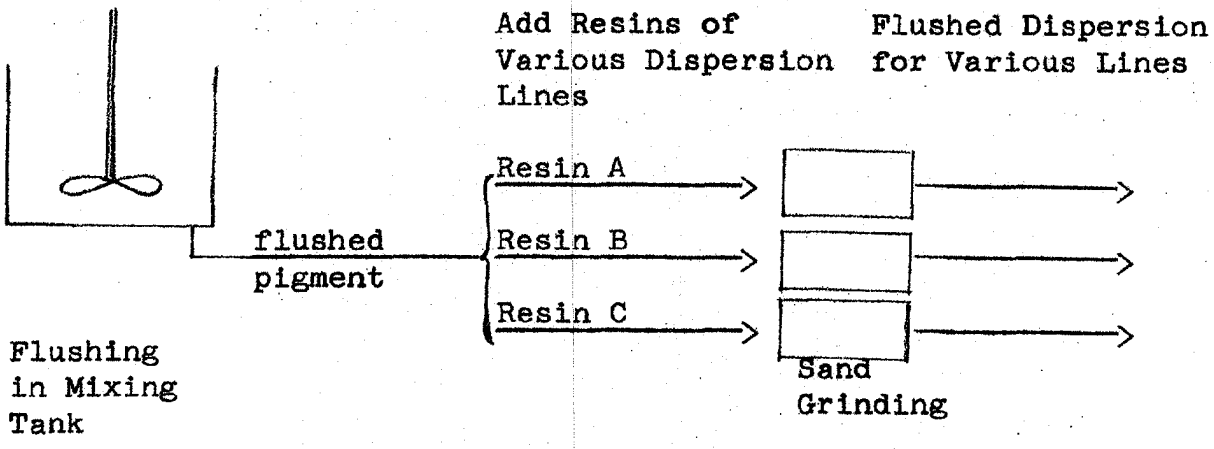
Our current process concept for flushing of organic pigments is illustrated schematically below:



The flushing is to be carried out in a low shear large mixing tank (equipped with heat jacket, condenser and vacuum) into a commonly used organic solvent (i.e., toluene). To the flushed pigment are added the resins of various dispersion lines and the resultant mixtures subject to sand grinding to break up the agglomerates which are present in the presscakes. This concept enables the flushing to be carried out in large quantity and the flushed pigment goes into various dispersion lines.

The economics of the flushing of organic pigments lies in (a) equal quality resulted from less grinding or (b) better utilization of pigment or (c) both.

The above process has been demonstrated successfully with the presscake of W765 in laboratory scale operation. Preliminary evaluation of the flushed W765 as a 308-line refinishes dispersion indicated that better dispersion quality could be obtained with equal amount of sand grinding or equal quality achieved with significantly less grinding. Most conventional sand ground dispersions of organic pigments used in the automotive and refinishes required two passes through the sand mill (as is the case for W765). Therefore, the key factor in comparing the flushing route v.s. conventional dispersion

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process is whether the combined savings from better grindability and/or improved pigment utility can justify the additional cost of flushing. This situation, which is characteristic of organic pigments, is now under evaluation in the refinishes as well as the automotive areas.

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TABLE I

SURFACE ENERGIES AND FLUSHABILITY OF PRESSCAKES

Presscake Code	W-Code	Contact Angle H_2O	Contact Angle Methylene Iodide	Surface Energy of Presscake (Erg./cm.^{2}) Non-polar	Polar	Total	% Surface Non-polarity	Flushability (into Toluene)
Transoxide Yellow 920-65	W-682	18	20	33.1	39.7	72.8	45.5	No
BT-427-D	W-558	61*	39*	29.1	20.2	49.3	59.0*	Yes
RT-695-D	W-300	60	36	30.2	20.4	50.6	59.7	No
RT-887-D	W-839	61	31	32.2	19.2	51.4	62.7	No
F-113-D	W-461	75	34	33.2	11.9	45.1	73.7	Yes
Irgazine Yellow 3RLT	W-673	77	25	37.2	10.1	47.3	78.6	Yes
RT-751-D	W-765	83	31	36.7	7.6	44.3	82.8	Yes

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TABLE II

FREE ENERGY OF FLUSHING AND FLUSHABILITY OF VARIOUS PIGMENTS

Dry Pigment	Surface Tension* of Pigment: Polar Component (γ_s^p)	Surface Tension* of Pigment: Non-polar Component (γ_s^d)	% Non-polarity	Calculated Free Energy of Flushing $\frac{\Delta G}{A}$ (Ergs/cm.^{2})	Flushed into N-decane	Residual Pigment in H_2O
W-300	24.1	27.8	54	16.5	No	Majority in H_2O
W-393	19.2	33.8	64	4.0	Yes	Noticeable
W-673	15.0	32.2	68	- 5.0	Yes	Noticeable
W-839	11.2	34.3	75	-15.2	Yes	Noticeable
W-537	10.1	39.4	80	-18.6	Yes	Noticeable
W-552	7.7	41.3	84	-25.6	Yes	Noticeable
W-765	6.2	35.8	85	-30.1	Yes	Negligible
W-505	6.9	40.0	85	-28.4	Yes	Negligible
W-560	2.4	49.2	95	-43.6	Yes	Negligible
W-588	2.1	50.7	96	-44.7	Yes	Negligible

Calculations of Free Energy of Flushing

$$\frac{\Delta G}{A} = \gamma_{so} - \gamma_{sw}$$

$$\gamma_{so} = \gamma_s + \gamma_o - 4\left(\frac{\gamma_s^d \gamma_o^d}{\gamma_s^d + \gamma_o^d} + \frac{\gamma_s^p \gamma_o^p}{\gamma_s^p + \gamma_o^p}\right)$$

$$\gamma_{sw} = \gamma_s + \gamma_w - 4\left(\frac{\gamma_s^d \gamma_w^d}{\gamma_s^d + \gamma_w^d} + \frac{\gamma_s^p \gamma_w^p}{\gamma_s^p + \gamma_w^p}\right)$$

γ_s^d and γ_s^p values for various pigments are given in columns (2) and (3)

$\gamma_o^d = \gamma_o = \gamma_{\text{n-decane}} = 23.9$; $\gamma^p_{\text{n-decane}} = 0$

$\gamma_w^d = \gamma^d_{\text{water}} = 21.8$; $\gamma_w^p = 51.0$; $\gamma_w = 72.8$

*These pigment surface tension values are taken from Report EX-70-22 (K. J. Brzozowski).

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TABLE III

TYPICAL FLUSHING PROCEDURE FOR TRANSOXIDE YELLOW (W-682) PRESSCAKE

Aqueous Phase	
Hilton-Davis Exp 920-65 Presscake	560.0
Water	960.0
Oil Phase	
Toluene	680.0
Bis(2EH)Hydrogen Phosphate (pre-dissolved)	17.0
——— Mix 20-30 minutes in a container with a propeller stirrer/decant H_2O; approximately 1200-1300 g. of H_2O can be removed by decantation.	
Add	
Toluene	217.5
H-257	217.5
A-B dispersant	130.0
---------- Centrifuged to remove residual H_2O and pigment agglomerates.	

The recovered dispersion was deflocculated and stable on aging. The composition of the flushed dispersion (coded 538E-115) was as follows:

	% by Weight
Toluene	61.1
H-257	15.0
H-5581	8.9
W-682	13.9
Bis(2EH)HP	1.1
	100.0

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TABLE IV

COMPARISON OF FLUSHED AND TWO-ROLL MILLED DISPERSION OF TRANSOXIDE YELLOW PIGMENT (W-682)

	Two-Rolled Milled Dispersion (912-G-60886)	Flushed Dispersion (538E-115)	References of Supporting Data
(I) Mill Base	(A) Flocculation Tendency		
	Deflocculated	Deflocculated	NB 538E-116 and NB 538E-193
	(B) Particle Size		
	Very fine, primarily in the range of 0.01-0.05μ	Coarser, primarily in the range of 0.05-0.20μ	Figure 3B and Figure 3C
	(C) Visual Appearance		
	Transparent and clean	Less transparent and milky at low angle of viewing	NB 538E-116 and NB 538E-193
	(D) Mill Base Stability		
	O.K.	O.K.	NB 538E-195
(II) Organosol	(A) Stability of Lacquer		
Lacquer - Solid Color	Unstable (became flocculated on aging)	Stable (no sign of flocculation)	NB 538E-195
	(B) Solid Color Drawdown		
	• Visual Appearance: Hazy	• Visual Appearance: Less hazy	NB 538E-195
	• Film X-Section by Electron Microscopy: Severely flocculated	• Film X-Section by Electron Microscopy: Flocculated	Figure 4A and Figure 4B
(III) Organosol	(A) Stability of Lacquer		
Lacquer - Metallic	Separation of Al flakes from color pigment	Less separation	NB 538E-195

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TABLE IV
Page 2

COMPARISON OF FLUSHED AND TWO-ROLL MILLED DISPERSION OF TRANSOXIDE YELLOW PIGMENT (W-682)
(Continued)

	Two-Rolled Milled Dispersion (912-G-60886)	Flushed Dispersion (538E-115)	References of Supporting Data
(III) Organosol (Continued)	(B) Sprayout Panels		
	• Two-tone: Better two-tone	• Two-tone: Slightly less two-tone	Panels 538E-14C and 14D; Figure 6 (OMR data)
	• Film X-Section by Electron Microscopy: Pigment moderately flocculated; equivalent overall appearance	• Film X-Section by Electron Microscopy: Pigment moderately flocculated; equivalent overall appearance	Figure 5A and Figure 5B
	• Effect of Aging: Aged lacquer gave reduced two-tone (~ 1 week)	• Effect of Aging: No significant effect on aging (~ 1 week)	Panels 538E-20A and 20B; Figure 7 and Figure 8

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FIGURE 1

ZETA POTENTIAL VS. pH OF LIQUID MEDIUM
(TRANSOXIDE YELLOW PRESSCAKE - W-682)

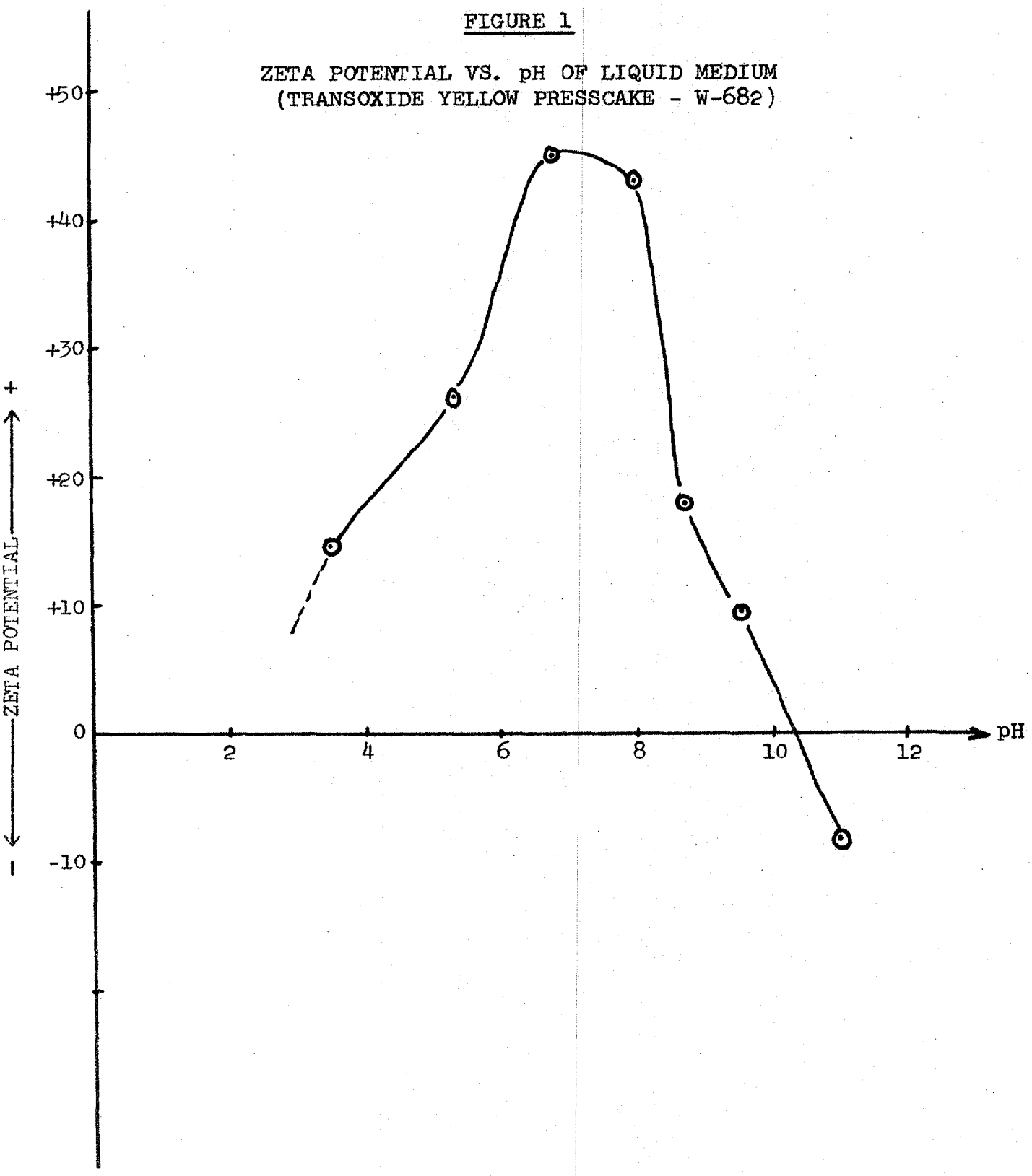

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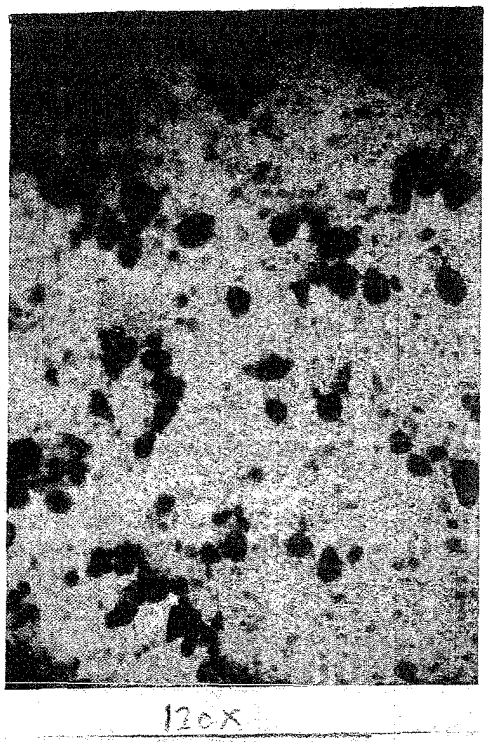
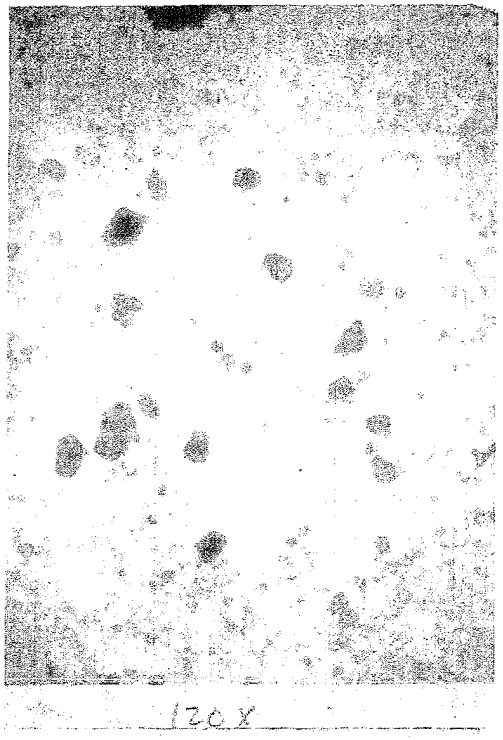
FIGURE 2

PIGMENT AGGLOMERATES IN PRESSCAKES (BT463P)



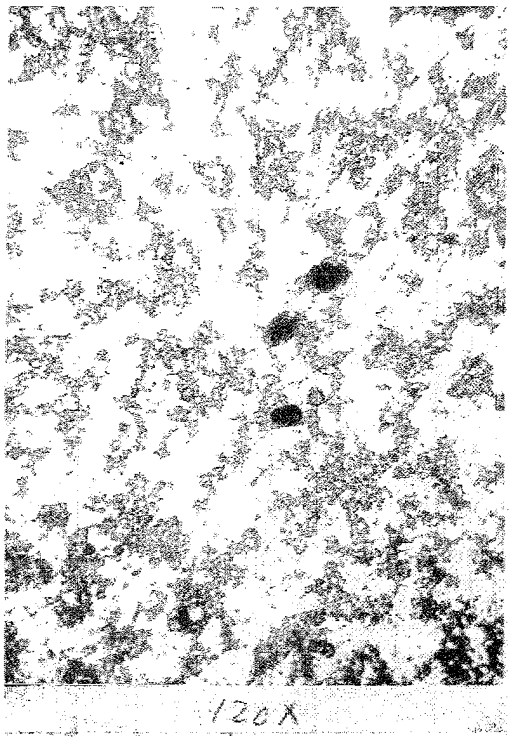
Mixing Equipment: Air driven stirrer 30 Minutes

% Agglomerates: 15-18%



Mixing Equipment: Cowles Dissolver 30 Minutes

% Agglomerates: 6-8%



Mixing Equipment: W & P Mixer 30 Minutes

% Agglomerates: ---

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FIGURE 3A

TRANSOXIDE YELLOW (W-682) PRESSCAKE
FROM HILTON DAVIS

SHOWING BASIC PARTICLE SIZE
AND SHAPE

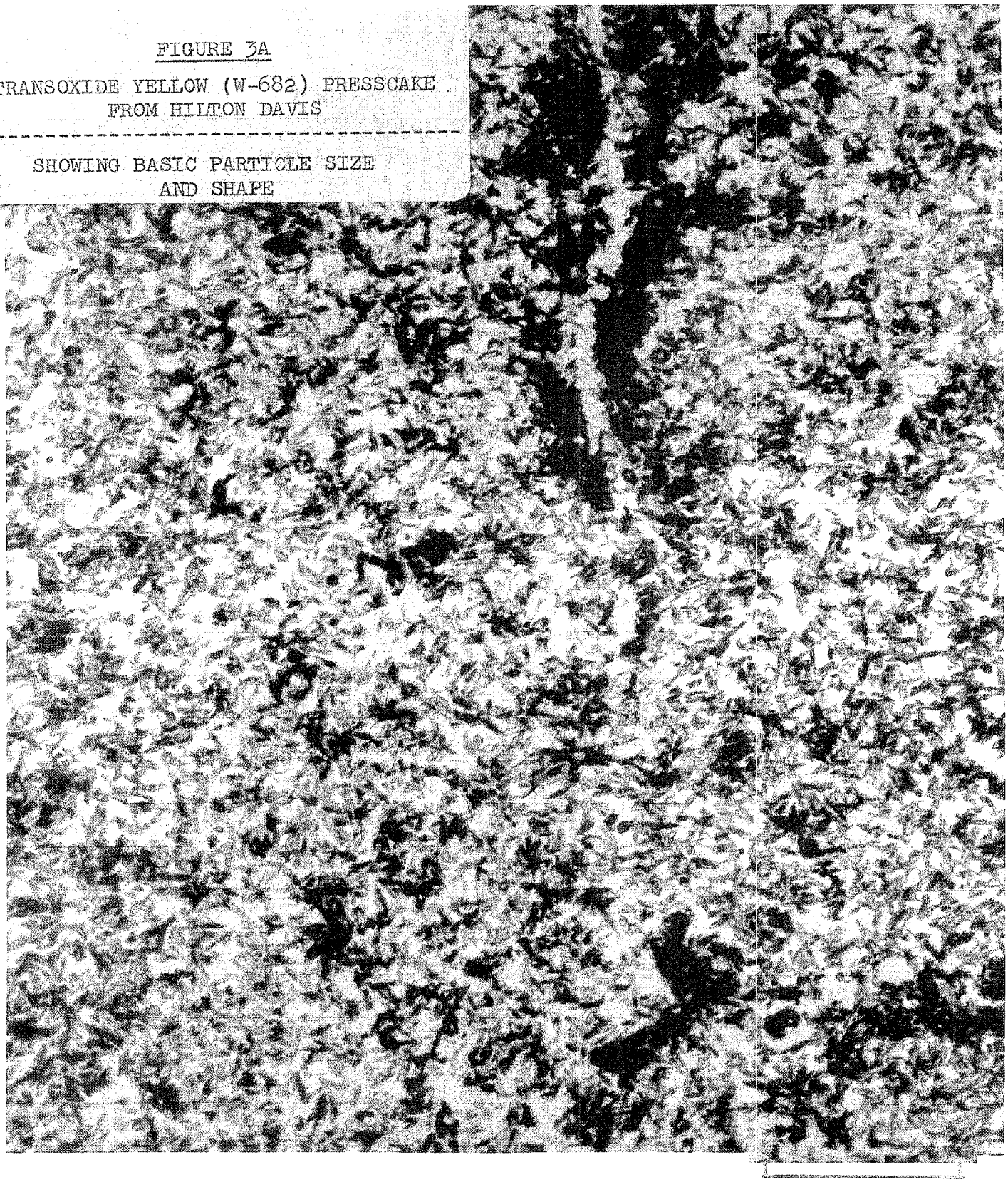

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FIGURE 3B

FLUSHED DISPERSION (W-682)

(538E-115)

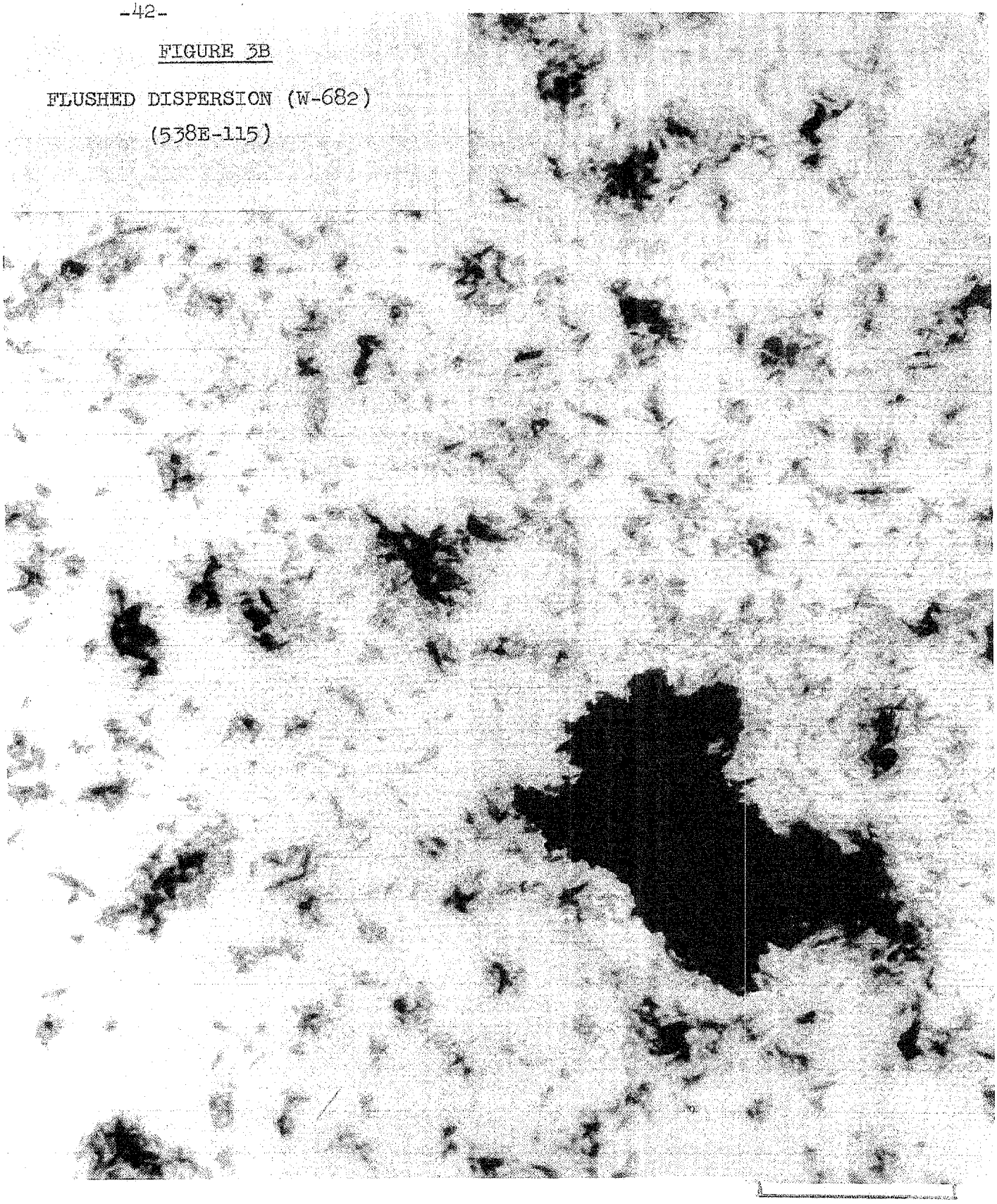

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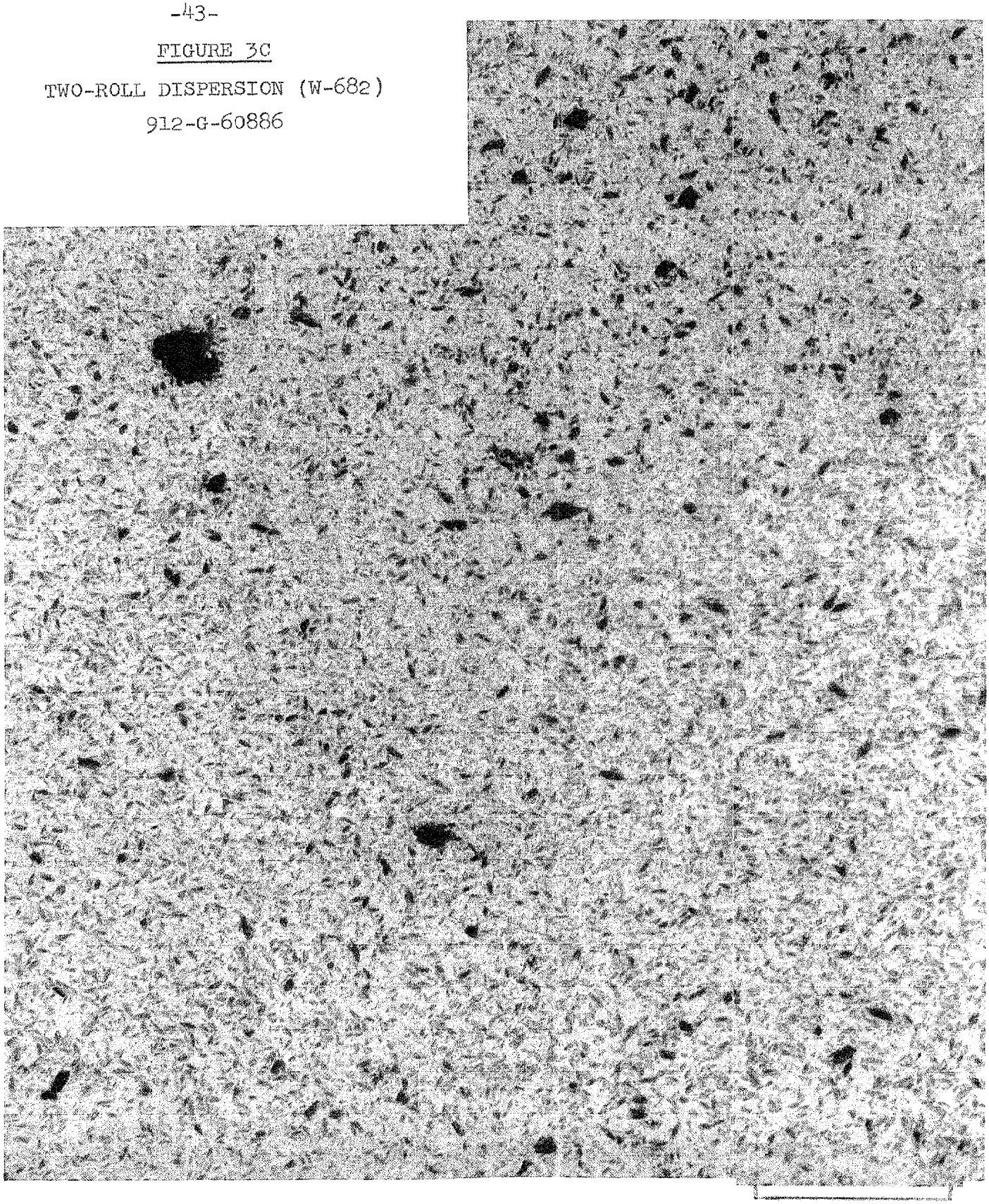
FIGURE 3C

TWO-ROLL DISPERSION (W-682)

912-G-60886



1μ

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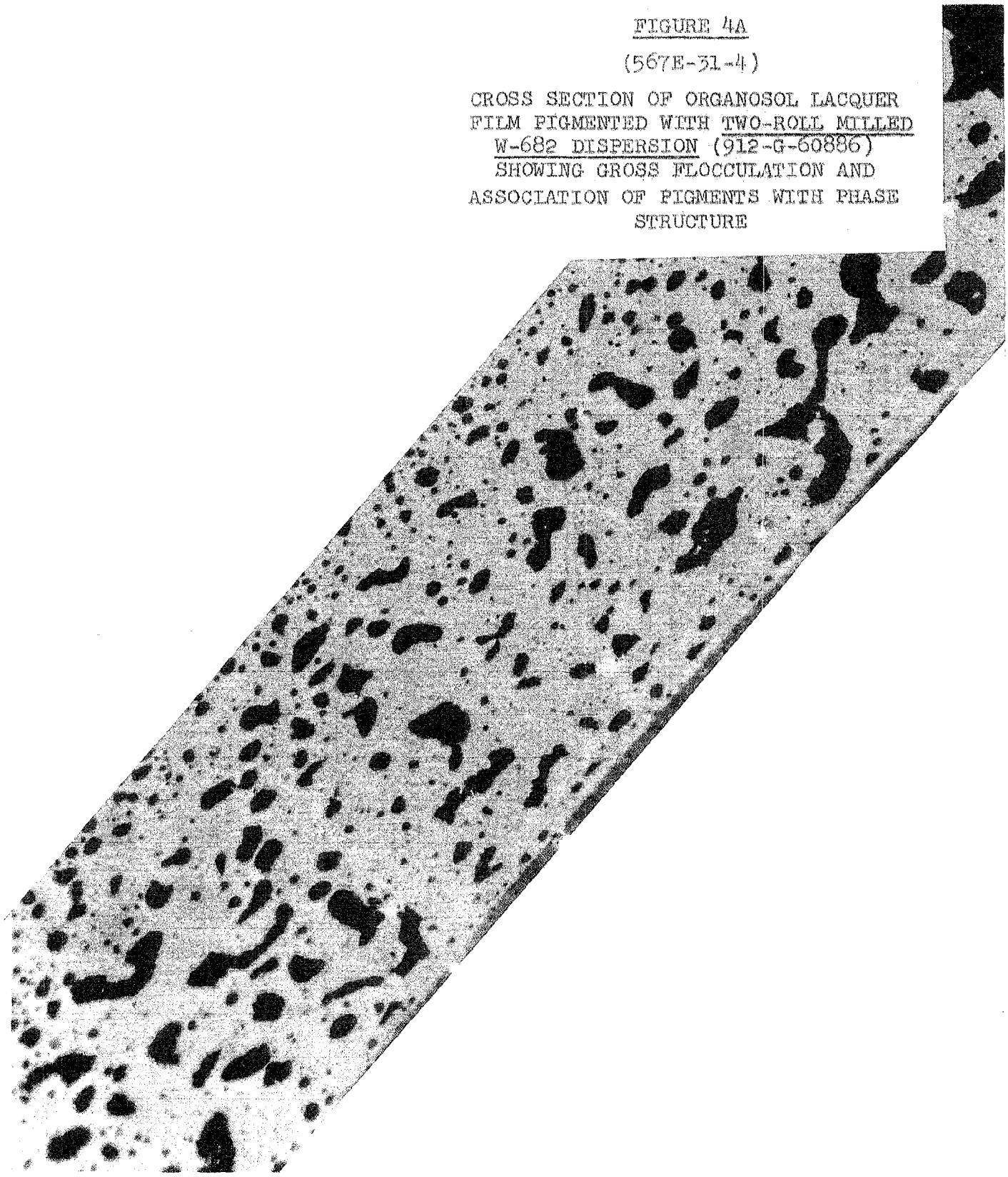
FIGURE 4A

(567E-31-4)

CROSS SECTION OF ORGANOSOL LACQUER FILM PIGMENTED WITH TWO-ROLL MILLED W-682 DISPERSION (912-G-60886) SHOWING GROSS FLOCCULATION AND ASSOCIATION OF PIGMENTS WITH PHASE STRUCTURE

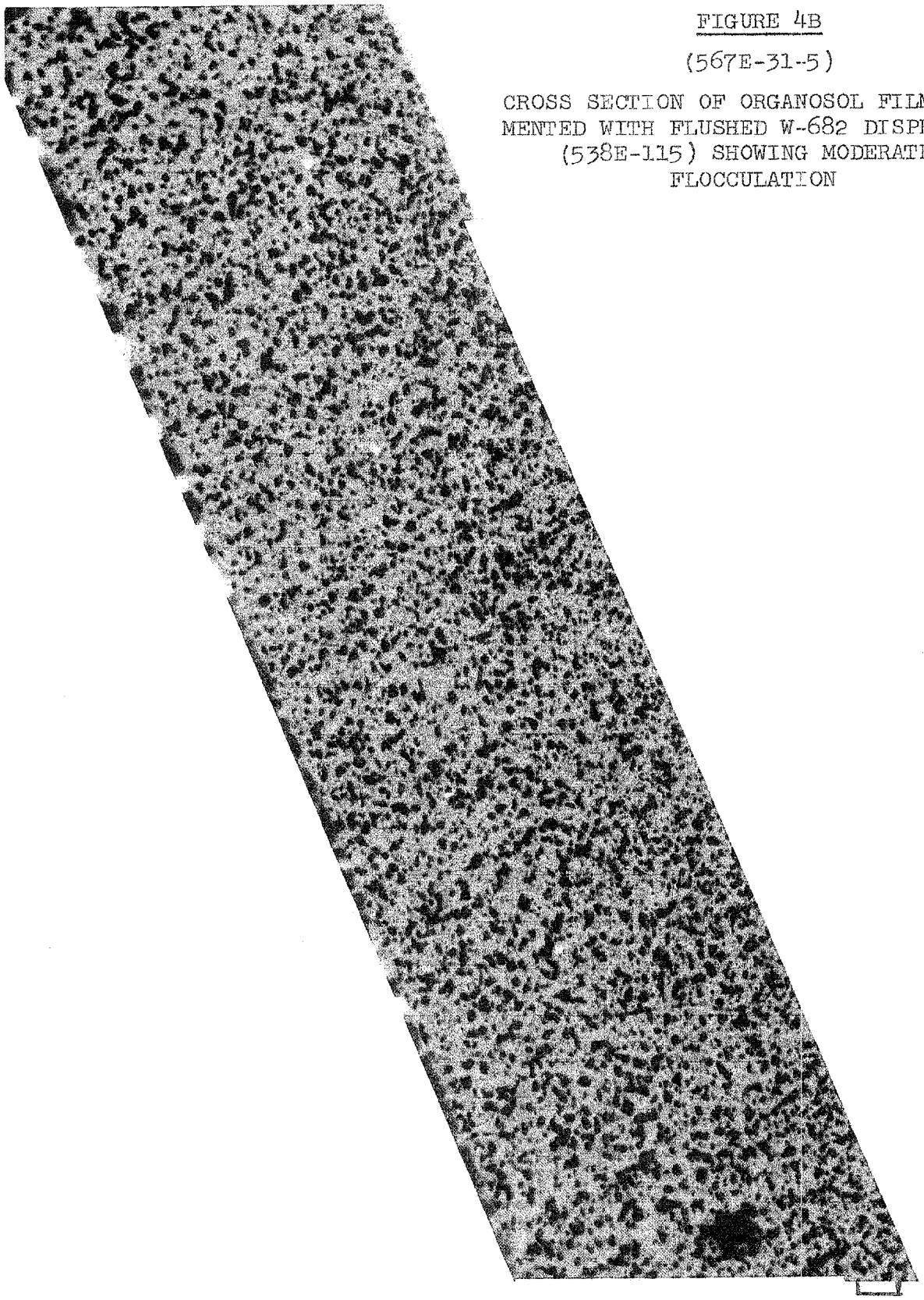


DUP030013928

FIGURE 4B

(567E-31-5)

CROSS SECTION OF ORGANOSOL FILM PIGMENTED WITH FLUSHED W-682 DISPERSION (538E-115) SHOWING MODERATE FLOCCULATION



DUP030013929

FIGURE 5A

CROSS SECTION OF METALLIC FILM BASED ON TWO-ROLL DISPERSION (W-682)

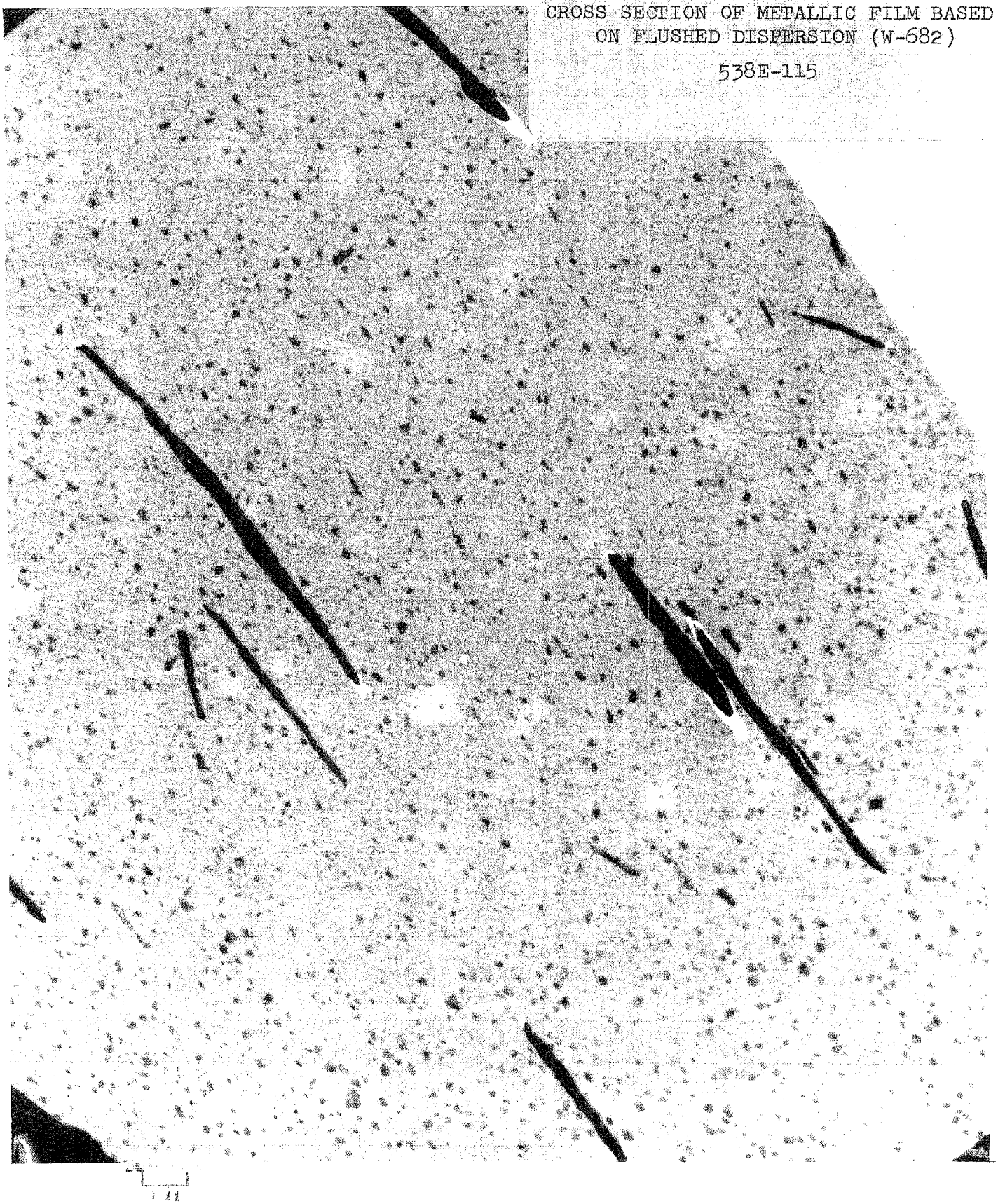
912-G-60886

DUP030013930

FIGURE 5B

CROSS SECTION OF METALLIC FILM BASED ON FLUSHED DISPERSION (W-682)

538E-115

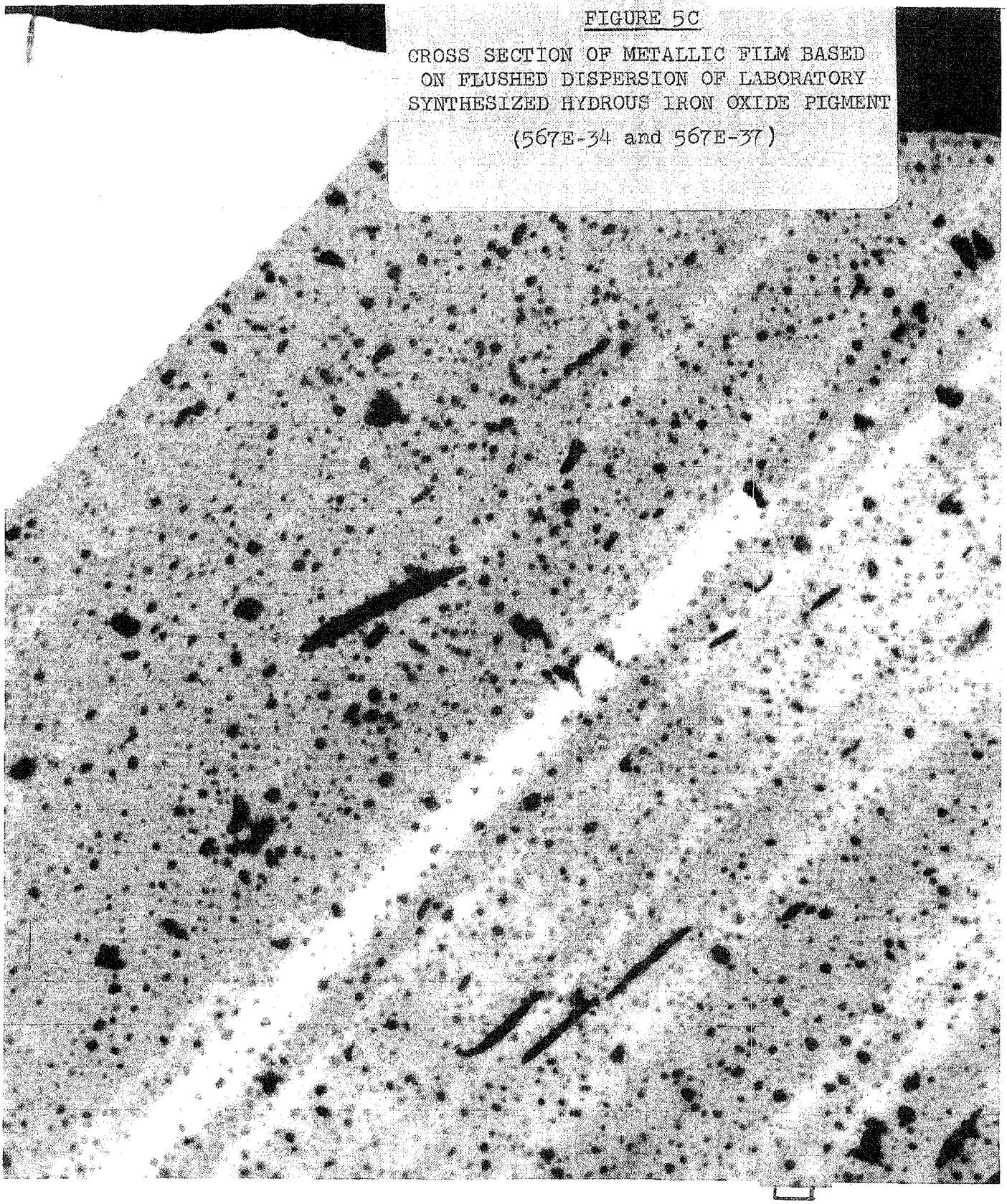


DUP030013931

FIGURE 5C

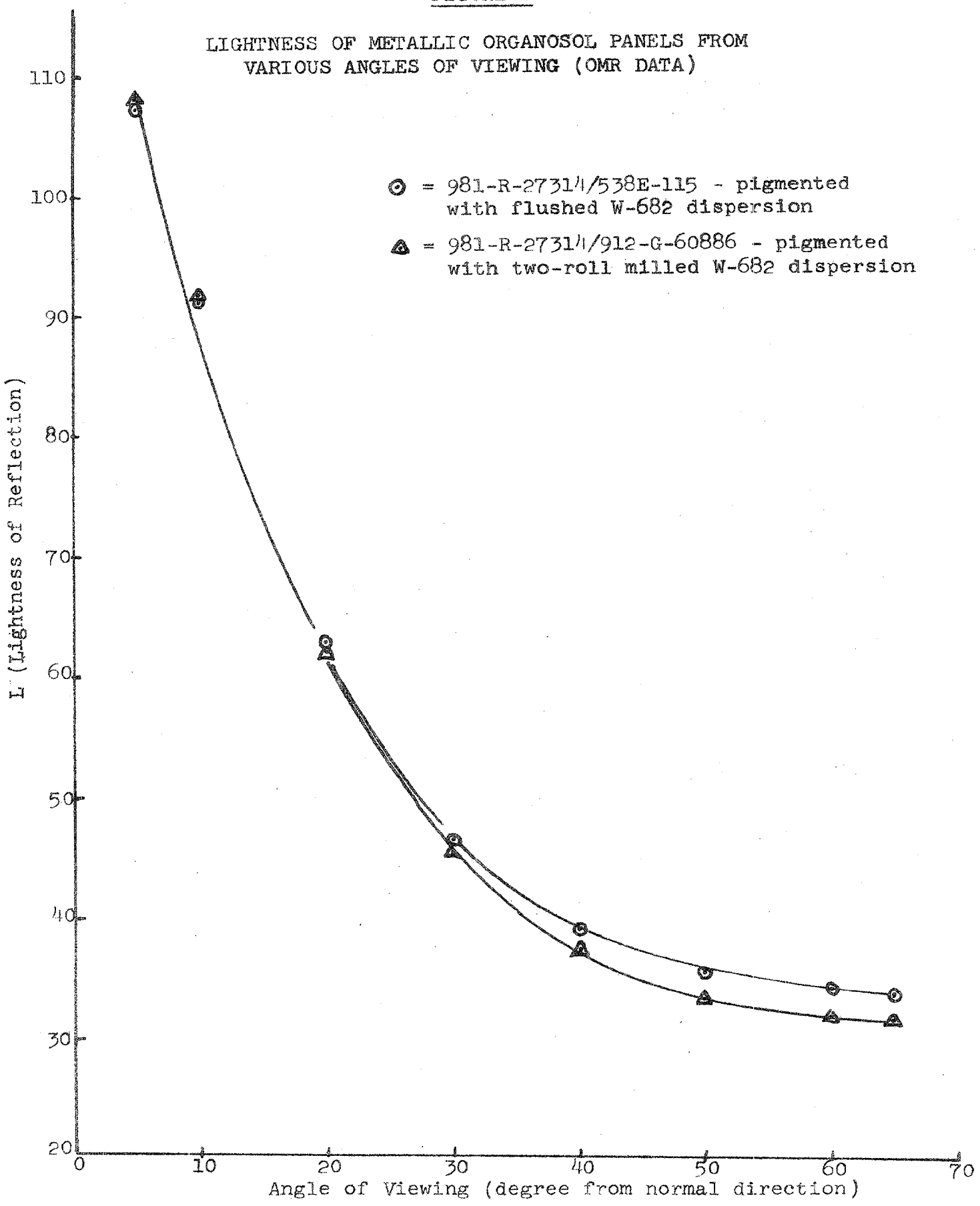
CROSS SECTION OF METALLIC FILM BASED ON FLUSHED DISPERSION OF LABORATORY SYNTHESIZED HYDROUS IRON OXIDE PIGMENT

(567E-34 and 567E-37)



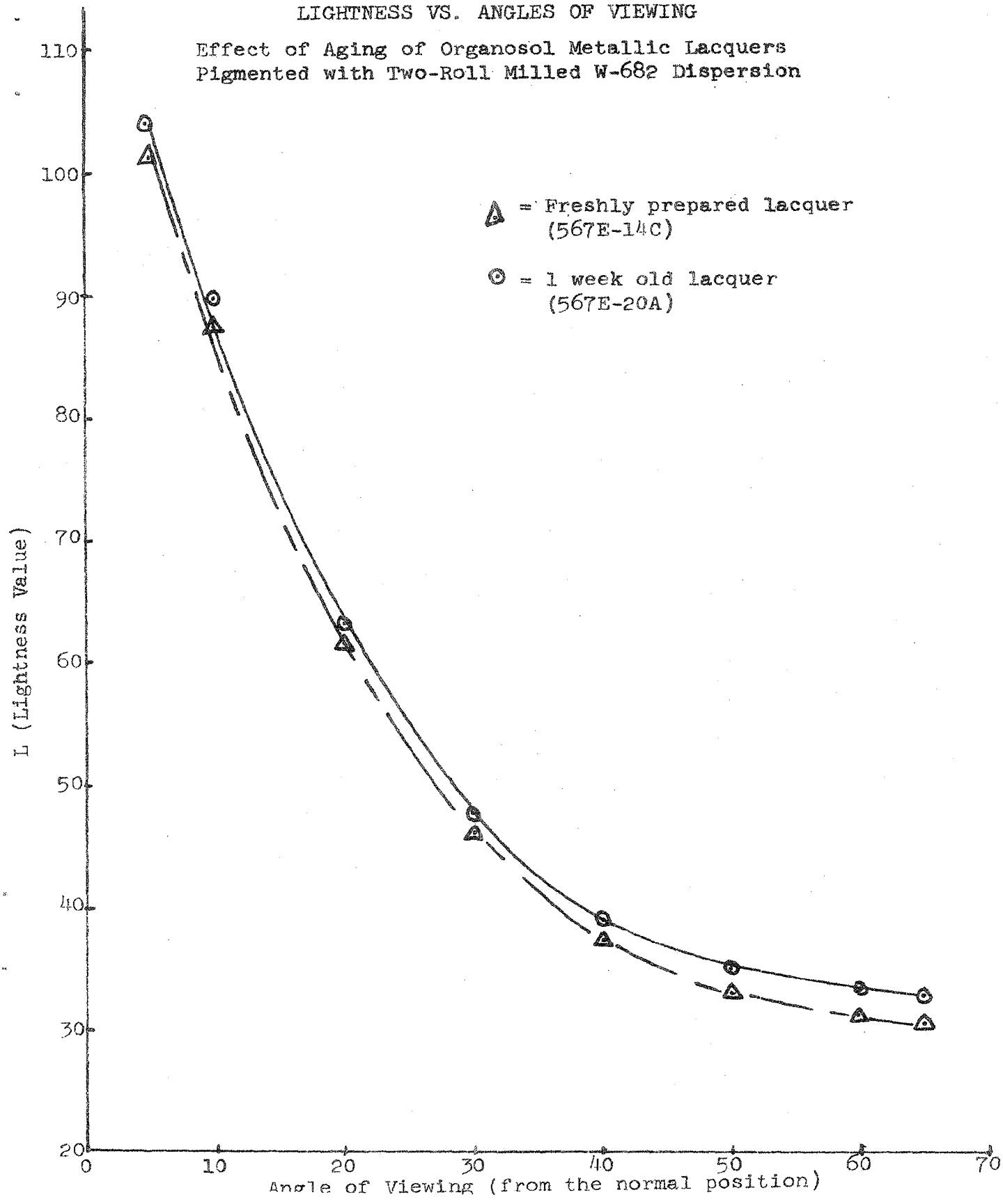
DUP030013932

FIGURE 6



DUP030013933

FIGURE 7

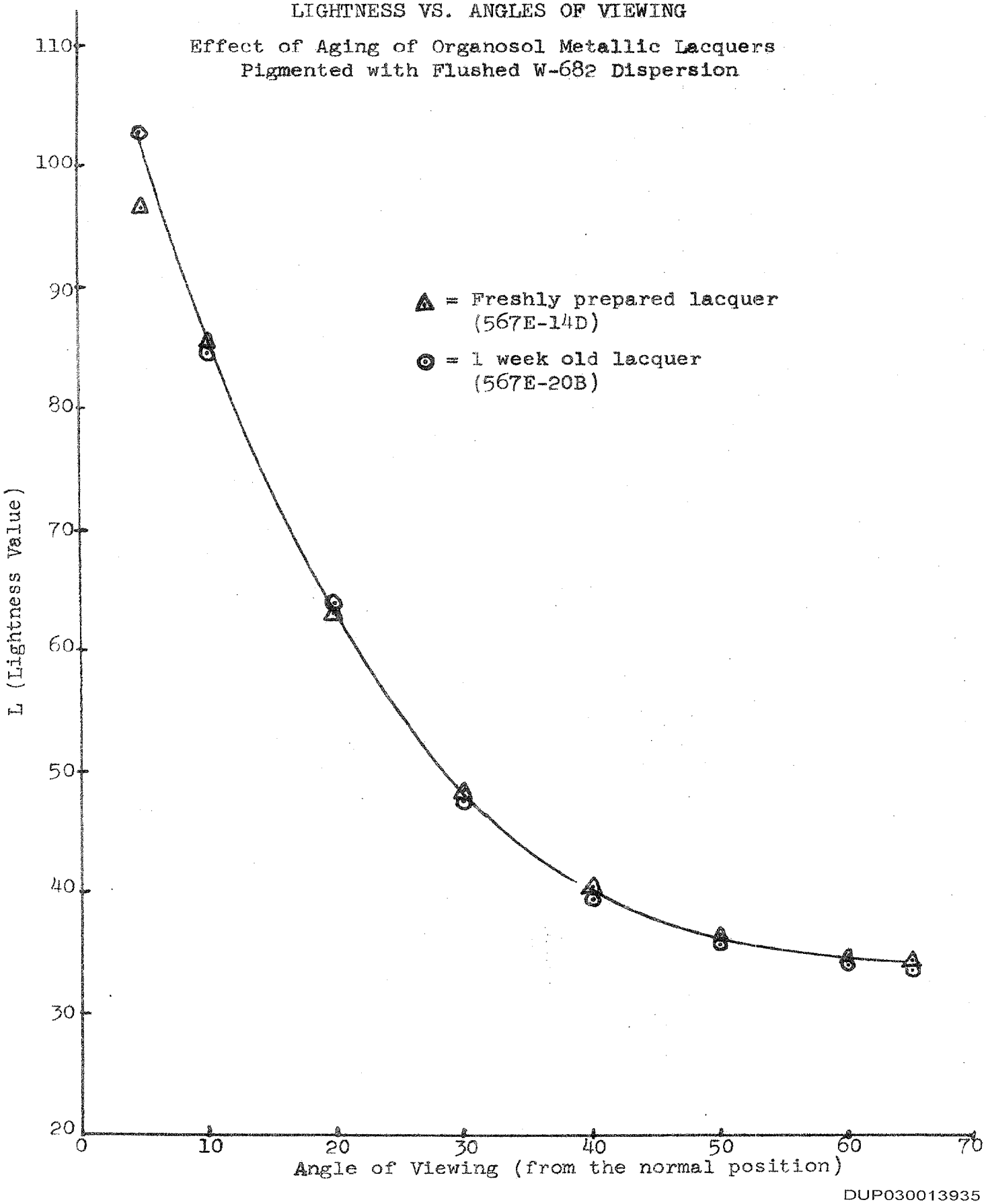


DUP030013934

FIGURE 8

LIGHTNESS VS. ANGLES OF VIEWING

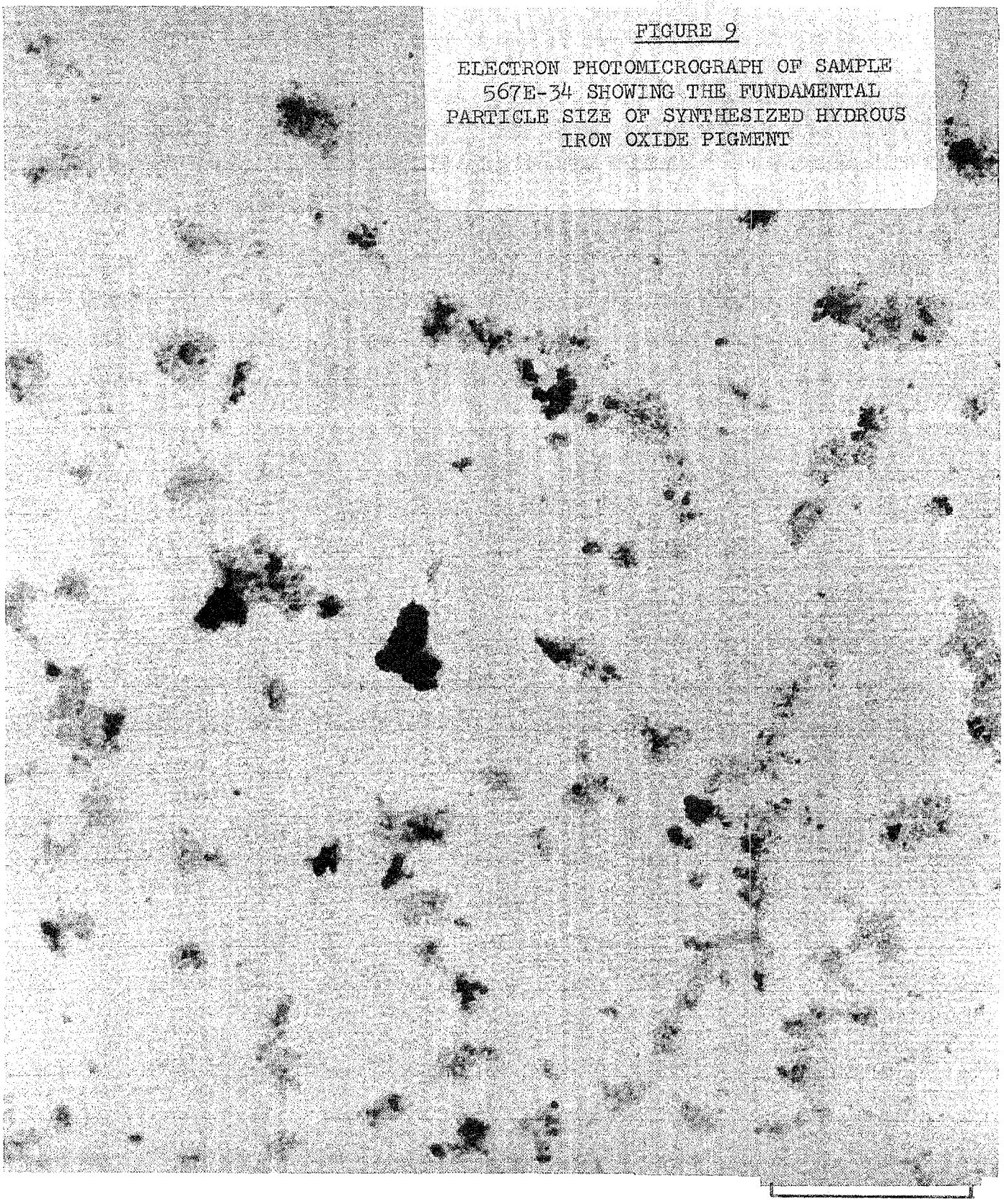
Effect of Aging of Organosol Metallic Lacquers Pigmented with Flushed W-682 Dispersion



DUP030013935

FIGURE 9

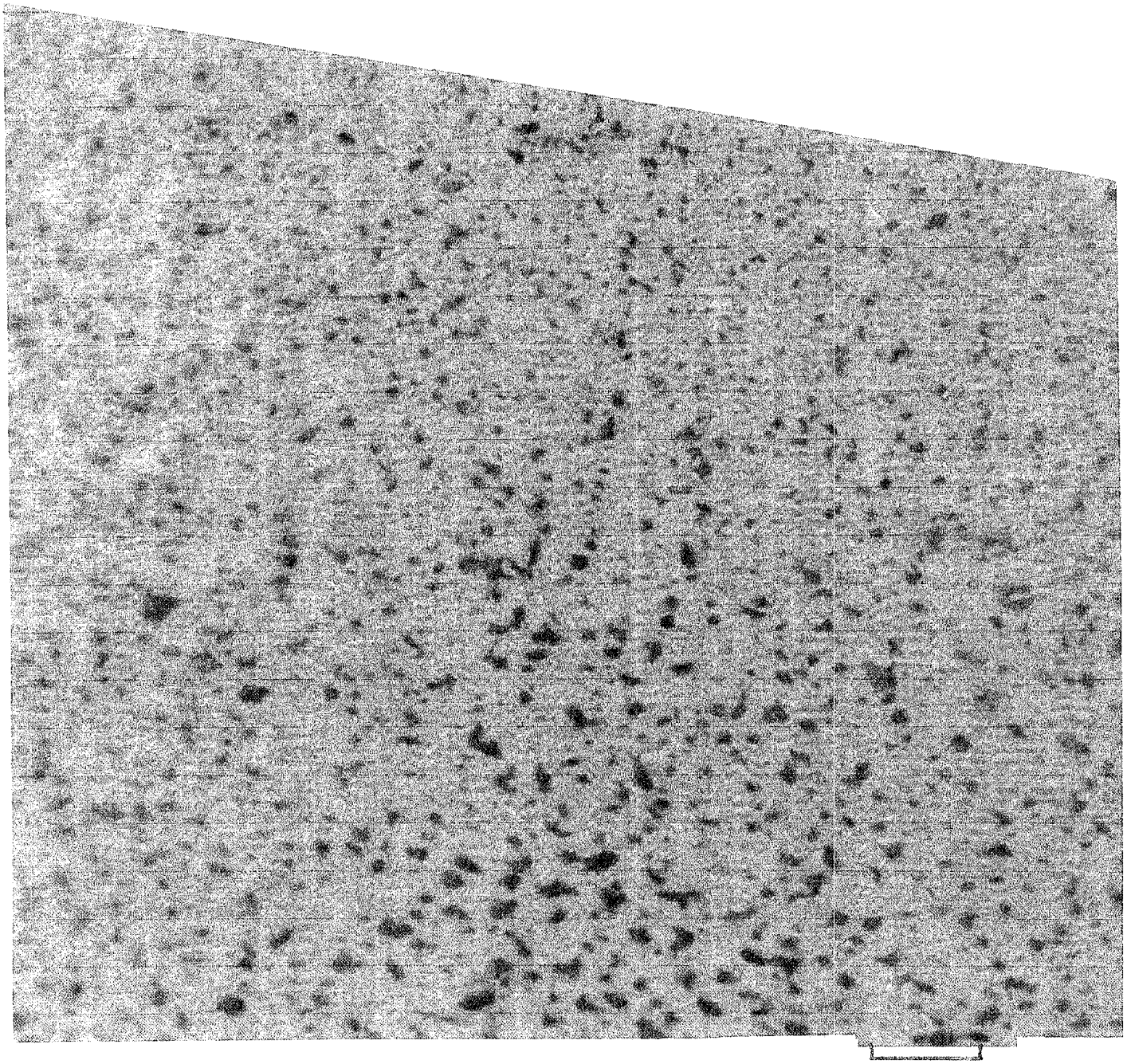
ELECTRON PHOTOMICROGRAPH OF SAMPLE 567E-34 SHOWING THE FUNDAMENTAL PARTICLE SIZE OF SYNTHESIZED HYDROUS IRON OXIDE PIGMENT



DUP030013936

FIGURE 10A

CROSS SECTION OF 567E-31-3 (ORGANOSOL LACQUER PIGMENTED WITH FLUSHED DISPERSION OF LABORATORY SYNTHESIZED HYDROUS IRON OXIDE PIGMENT) SHOWING TOP PORTION OF THE FILM

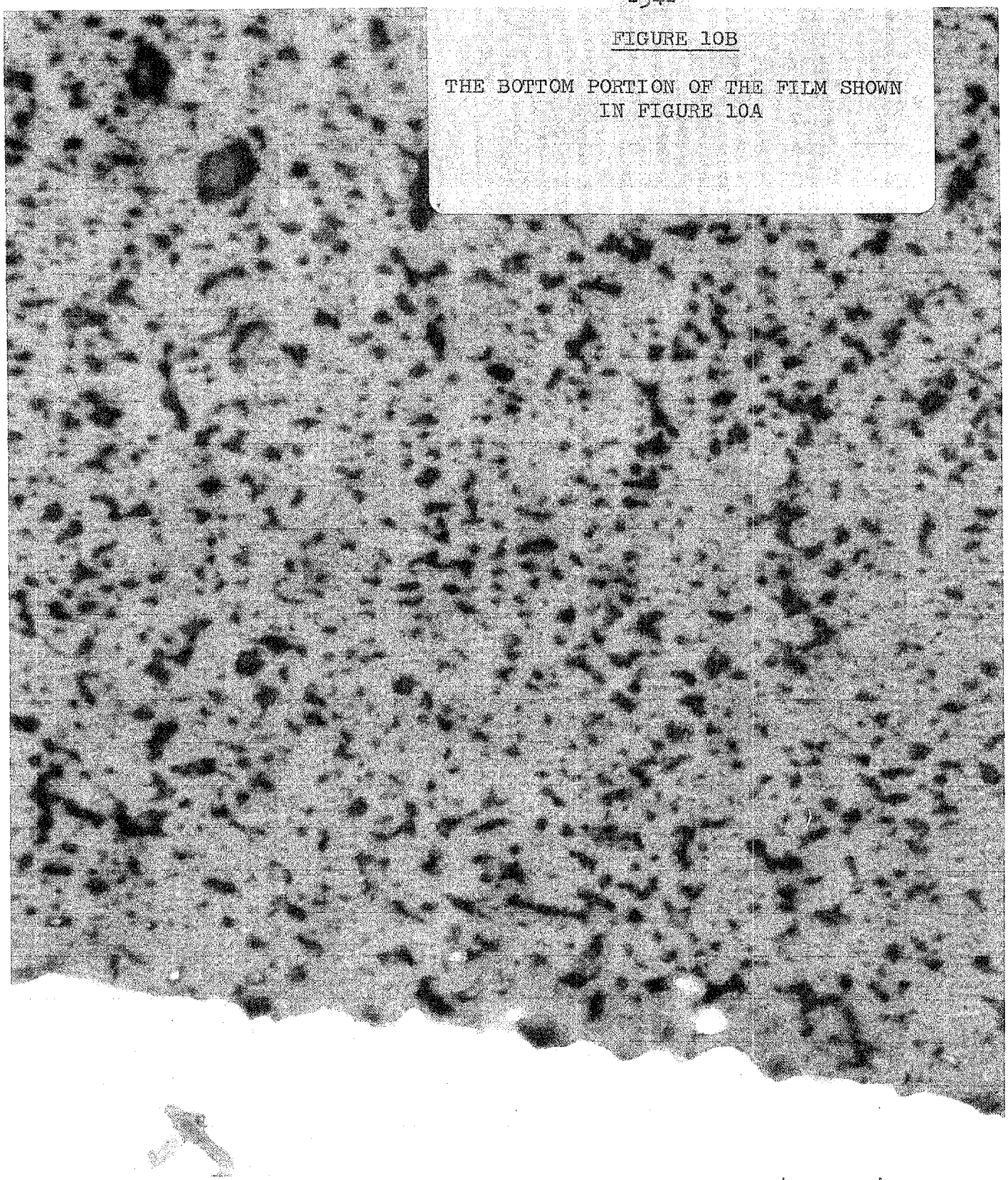


1μ

DUP030013937

FIGURE 10B

THE BOTTOM PORTION OF THE FILM SHOWN IN FIGURE 10A



DUP030013938

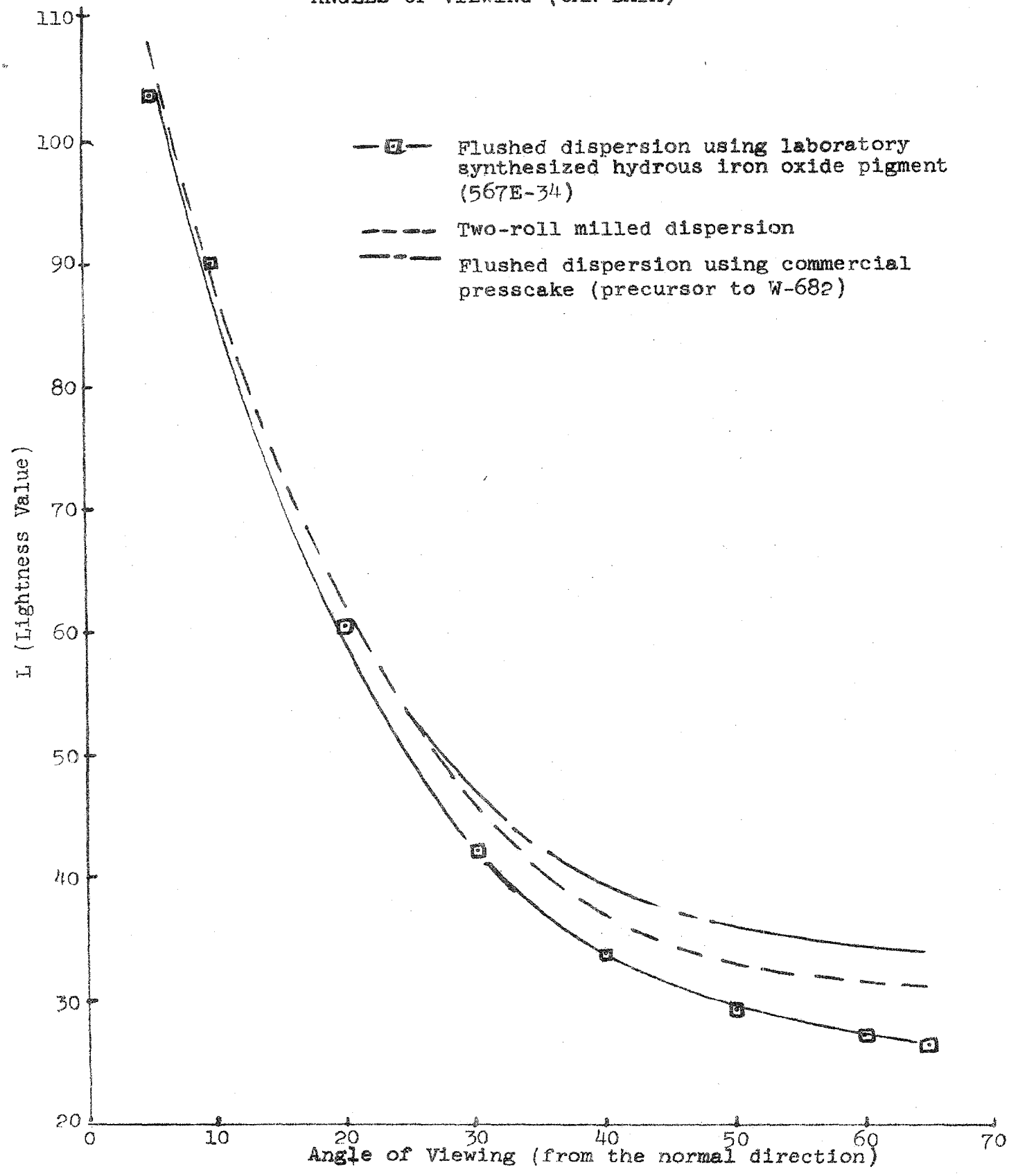
FIGURE 11

See Page in body of report

DUP030013939

FIGURE 12

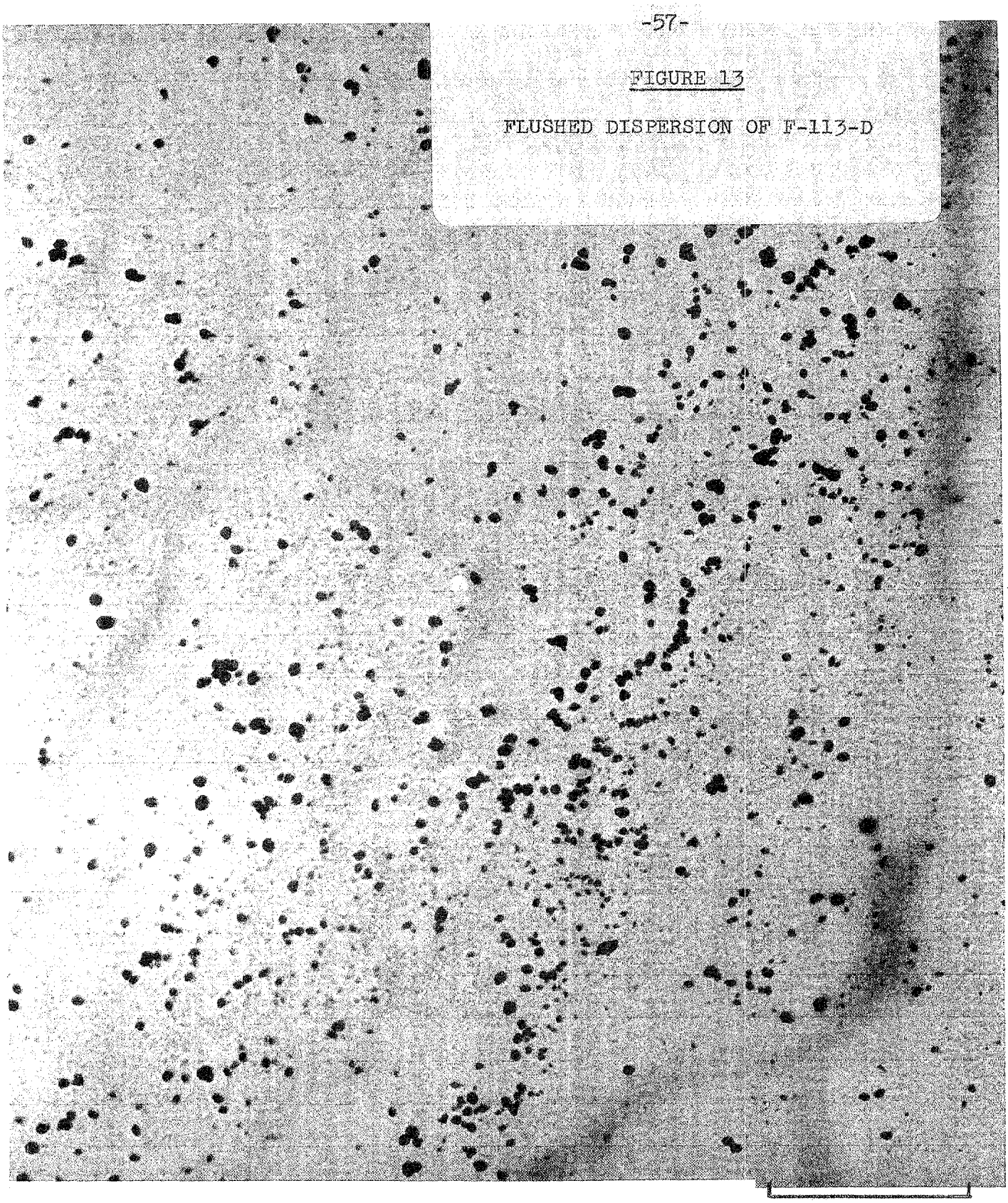
LIGHTNESS OF METALLIC ORGANOSOL PANELS AS A FUNCTION OF ANGLES OF VIEWING (OMR DATA)



DUP030013940

FIGURE 13

FLUSHED DISPERSION OF F-113-D

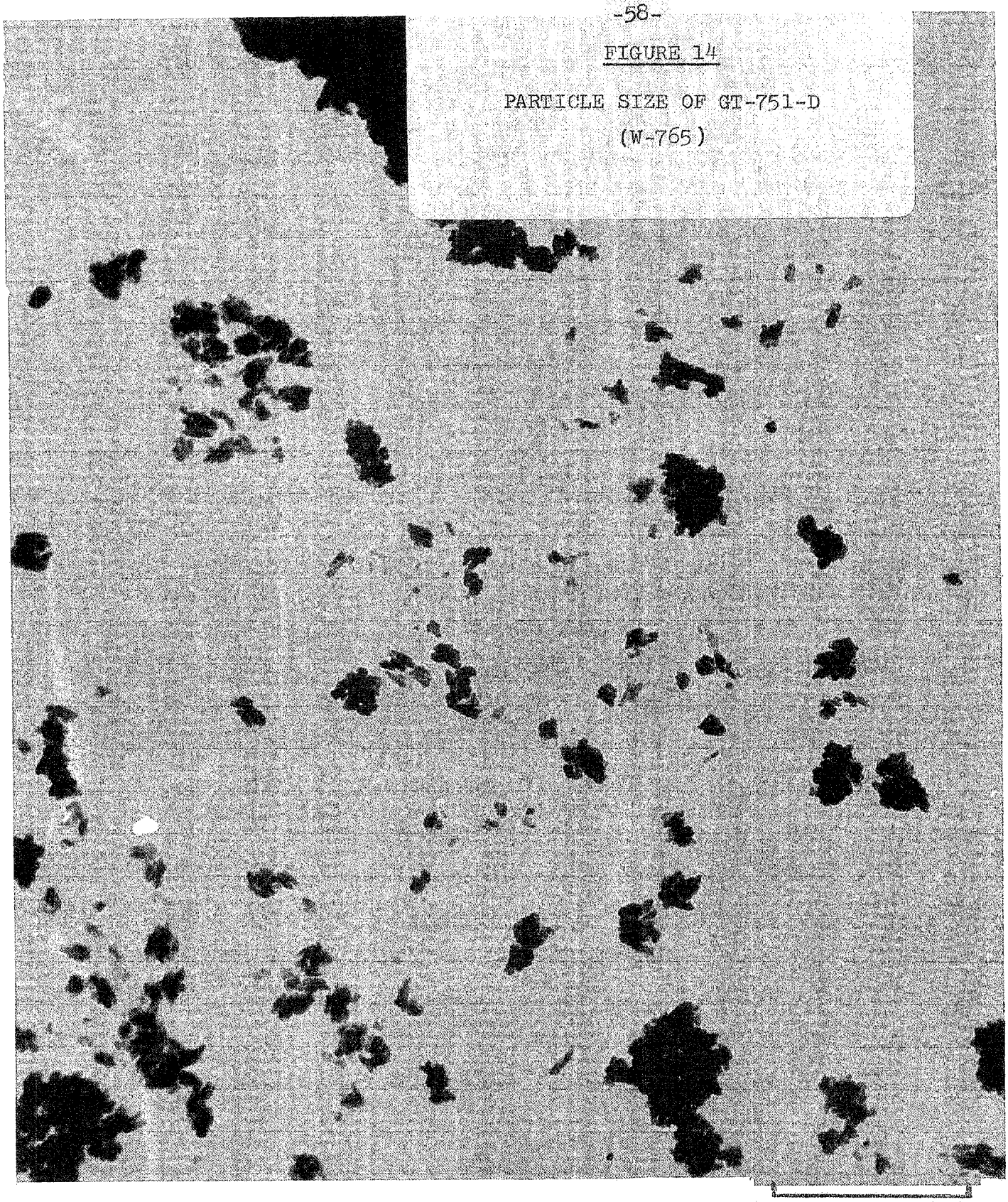


DUP030013941

FIGURE 14

PARTICLE SIZE OF GT-751-D

(W-765)

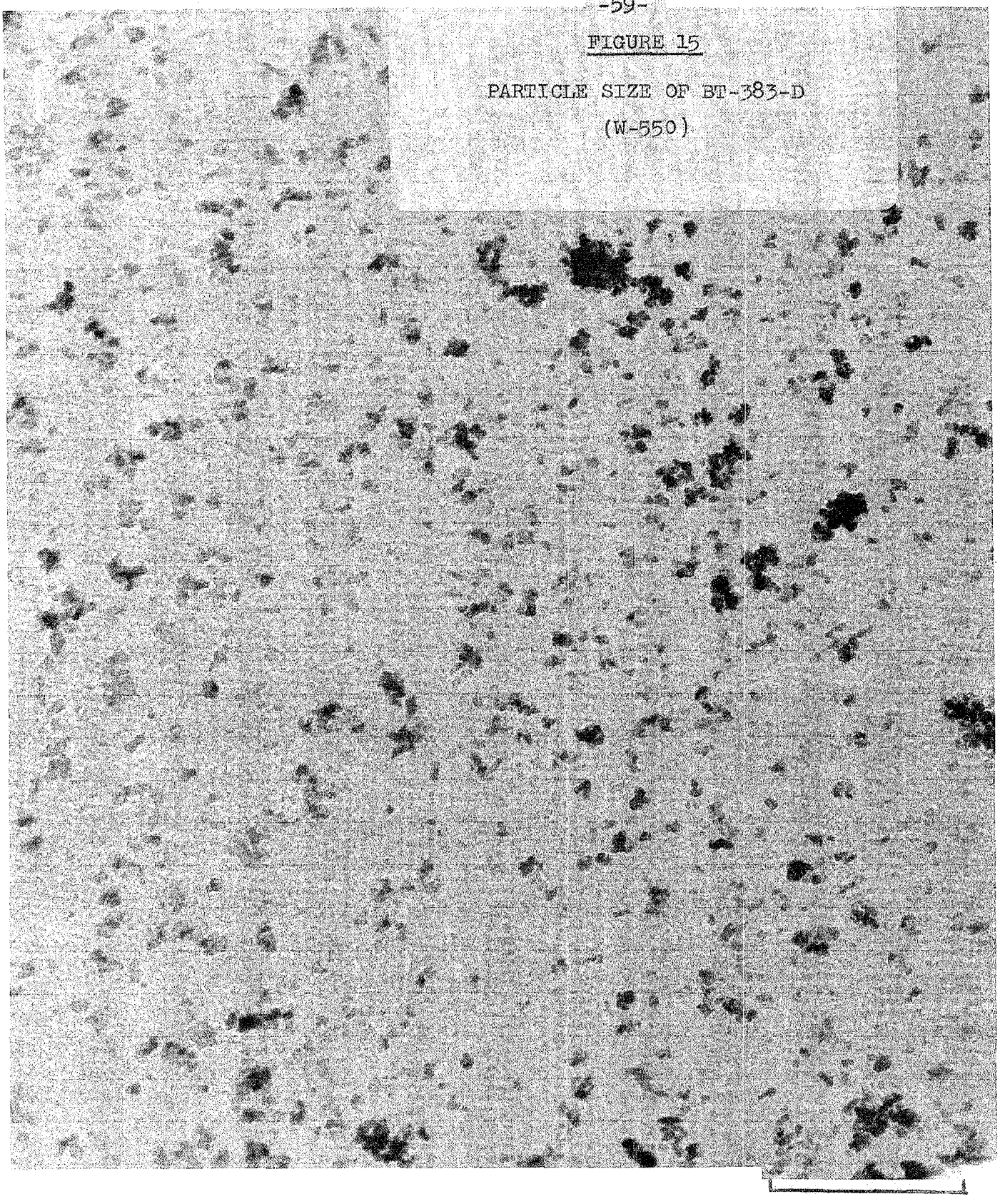


DUP030013942

FIGURE 15

PARTICLE SIZE OF BT-383-D

(W-550)



1μ

DUP030013943

APPENDIX I

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Not Indexed
File: 611331

Experimental Station
April 21, 1971

F. N. JONES
F & F DEPARTMENT
EXPERIMENTAL STATION

MANUFACTURING COSTS OF MILL BASES VIA "FLUSHING"

A preliminary study of the manufacturing costs of mill bases via "flushing" was made by J. P. Herring, Engineering Dept., at my request. In accordance with the initial leads developed in the "Pigment Flushing" program, two "flushing" processes received consideration.

Case I was a low shear mixer flushing followed by decantation and vacuum distillation; Case II, a low shear mixer flushing followed by continuous centrifugation. A brief description of the basic procedures for the two cases and the estimated manufacturing costs are given in the following table.

Description	Case I	Case II
Manufacturing Procedures:	(1) Charge presscake, organic liquids, transfer agent, etc. into the mixing tank.	(1) Same.
	(2) Continue agitation until "flushing" is completed.	(2) Same.
	(3) Stop agitation. Let stand until water forms a separate phase.	(3) Pump mixture through a continuous centrifuge. Water & coarse particles are simultaneously separated from the pigment dispersion.

DUP030013944

The Experimental Station Special Services Lab has two continuous centrifuges of the type described. Arrangement can be made for temporary use of their equipment.

A sample of flushed transoxide yellow dispersion obtained by the Case II process has been sent to Flint (J. G. King) for evaluation. Pending the results of King's evaluation, a course of action will be recommended.

I. C. Chu

I-Cheng Chu

ICC/mcc
4/21/71

DUP030013945

Description	Case I	Case II
	(4) Decant water.	(4) ---
	(5) Vacuum distill residual water.	(5) ---
	(6) Packaging.	(6) Packaging.
Manufacturing Cost ($/lb., pigment):	$0.20-0.35	$0.17-0.25
20% Return on Investment:	$0.19	$0.19
Total:	$0.39-0.54*	$0.36-0.44*

*These manufacturing costs are to be compared with $1.30-1.60/lb. pigment by the two-roll milling procedure which is required for most high quality dispersions.

It is assumed that the flushing operation can be carried out in the 1000-gal. mixing tank now available at the Parlin Plant. Hence, for Case I, no new investment will be needed. However, for Case II, new investment in the continuous centrifuge will be required. The reduced manufacturing cost for Case II is the result of labor savings due to the shorter batch cycle and reduced operator attention. ROI is assumed equal in both cases, since the new investment required in Case II is approximately off-set by the reduced allocated investment. Case II is particularly suitable for pigments such as iron oxides because centrifugation permits removal of the aggregates as well as residual H_2O. (Presscakes of iron oxide pigments already contain significant amounts of aggregates.)

The prices of small continuous centrifuges suitable for the described type of operation range from $10,000-15,000. These centrifuges would have a capacity of 5-25 gallons/min. which would be adequate for manufacture of medium batches of mill bases.

DUP030013946

APPENDIX II

SUMMARY OF PRIOR ART ON "FLUSHING"

U.S. 2,140,745 - Du Pont Co., 12/20/1938

This patent relates to improved cellulose coating compositions and a process for direct transfer of pigment particles from a water suspension to a cellulose derivative vehicle.

Process:	W & P mixer followed by tray drying or vacuum drying until the residual H_2O is less than 3%.
Vehicle System:	Cellulose nitrate.
Transfer Agent:	Presumably, dibutyl phthalate, etc.
Pigments:	Chinese blue pigment pulp; maroon pigment pulp; lead chromate pulp; carbon black dry pigment, etc.

U.S. 2,112,222 - InterChemical Company, 9/21/1933

This invention relates to a method of manufacturing pigments dispersed in oil and to the product thereof. The flushing of pigments from wet presscakes into organic media and the separation of water from the oil curd containing the pigments are improved by using a soluble emulsifier (i.e., soap) followed by a precipitant.

Soluble Emulsifiers:	Sodium or potassium soaps of oleic acid, stearic acid, recinoleic acid, etc.
Precipitants:	Barium, calcium, magnesium, aluminum, strontium and lead salts.
Organic Media:	Linseed varnish

DUP030013947

U.S. 2,112,222 - InterChemical Company, 9/21/1933 (Cont'd.)

Pigments:	Para toner, lithol R Red, and Prussian Blue
Process:	The flushing is carried out in a simple mixer; the final drying in a steam jacketed container.

U.S. 2,335,760 - Du Pont Co., 11/30/1943

This patent discloses the direct incorporation of a hydrous iron oxide pigment into a cellulose derivative vehicle by flushing.

Process:	Kneading in a M & P mixer followed by (a) sheeting the pigmented mass through a loosely set steel rolls and tray drying, (b) vacuum drying in the M & P mixer.
Vehicle System:	Cellulose nitrate derivations.
Transfer Agents:	Presumably blown castor oil and dibutyl phthalate.
Pigment:	Hydrous iron oxide presscake freshly prepared.

U.S. 2,964,418 - National Lead Co., 12/13/1960

This patent discloses a process for flushing a basic cadnium salt of a fatty acid.

Process:	Vibratory mixing apparatus or heavy duty Baker-Perkins mixer followed by vacuum evaporation.
Organic Phase:	Plasticizers (such as dioctyl phthalate); mineral oils; polyester of adipic acid and glycol; soybean oil, etc.

DUP030013948

U.S. 2,964,418 - National Lead Co., 12/13/1960 (Cont'd.)

Transfer Agents:	Not mentioned specifically; increased temperature facilitated phase transfer; aliphatic alcohols also were used.
Materials to be Flushed:	Cadnium salt of fatty acids such as cadnium caprylate and cadnium laurate, etc.

U.S. 3,431,130 - Chemetron Corporation, 3/4/1969

Dry pigments of fine particle size and dispersibility are produced without agglomeration by dehydrating a presscake with a low boiling organic solvent and combining with a solid salt dispersing agent which is thermally stable under the conditions of mixing but volatile when heated up.

Process:	Presscake was washed with a low boiling solvent until most water is removed from the pigment. The solvent presscake was mixed with a solid salt dispersing agent in a ball mill. The resulting mixture was heated up to the decomposition temperature of the dispersing agent and thereby leaving dry pigments in a non-agglomerated state.
Thermal Decompassable Dispersing Agents:	Ammonium carbonate.
Pigments:	CPC blue & green; indanthrone; quinacridone, etc.

DUP030013949

U.S. 3,508,943 - Koppers Co., 4/28/1970

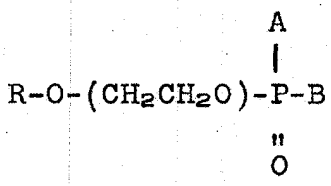
This patent describes the flushing of nacreous pigment crystals such as crystals of lead hydrogen arsenate by using a polyethylene phosphate as flushing agent.

A typical examples is given as follows: A thickened paste of lead hydrogen arsenate platclet crystals was stirred with a mixture consisting of dioctyl phthalate and a small percentage of polyethylene phthalate as flushing agent. With gentle stirring at 80°C, all of the crystals were transferred to the dioctyl phthalate phase. After separation of free water, the residual entrained H_2O was expelled by centrifugal separation at 2000G.

Process: As described above, involves mixing/centrifugal separation of residual water.

Organic Phase: Dibutyl phthalate, dioctyl phthalate, nitro cellulose solution, organic solvents--hydrocarbons, esters, ketones, alcohols, etc.

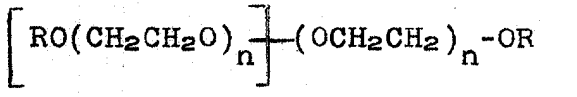
Transfer Agents:



Where R = Alkyl, alkenyl. Alkyl phenyl radicals in which the alkyl portion has C_4-C_{18}.

N = 3-15

A & B are selected from group OH and



DUP030013950

U.S. 3,508,943 - Koppers Co., 4/28/1970 (Cont'd.)

Applicable Pigments: Lead carbonate, lead hydrogen arsenate, lead hydrogen phosphate and bismuth oxychloride.

British 1,212,346 - ICI, 11/11/1970

This patent discloses an improved process for "flushing" of pigments from dispersions in aqueous media to non-aqueous media.

The process consists of (a) ball milling the press-cake in water with a water-soluble salt of a water-insoluble carboxylic acid (e.g. potassium linoleate); (b) the aqueous dispersion from (a) being mixed with an alkyd resin; (c) the "flushing" being carried out in a heavy duty mixer with the assistance of a precipitating agent (i.e., acetic acid) which converts the water-soluble salt into a water-insoluble form depositing on the pigment particles; flushing and water separation follow immediately; (d) the flushed dispersion still contain significant amount of water (~20% on pigment weight).

The following patents are not directly related to "flushing" but contain comments and references on "flushing":

U.S. 3,565,656 - Allied Chem. Corp., 2/23/1971

The patent relates to a soft, easily dispersible iron oxide pigment obtained by taking i.e., precipitating freshly prepared ferrous/ferric hydroxide together with aluminum hydroxide. It also contains information concerning the art of flushing of iron oxides.

U.S. 3,533,934 - Mearl Corporation, 10/13/1970

This patent discloses the method for dehydrating nacreous pigment platelets. The process involves washing the presscakes with water-miscible solvent and collecting the platelet pigments by settling, the settling rate being increased by using current through the dispersion.

It also contains a review of flushing methods for the nacreous platelet pigments.

DUP030013951

ABSTRACT

The important factors governing pigment flushability and guidelines for selection of flushing aids are discussed.

A simple and economical process for flushing transoxide yellow pigment into organic phase is described. The flushed dispersion could be used in organosol lacquers.

The influence of fundamental particle size on film transparency and metallic two-tone was elucidated.

DUP030013952

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