KM-70-9 CPC - TWO-STAGE DROWNING PROCESS DEVELOPMENT By: W. L. Monson 6/1/69 - 3/1/70

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CPC - TWO-STAGE DRUMMING
PROCESS DEVELOPMENT

W. L. Monson 6/1/69 - 3/1/70

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NEWPORT PLANT

PIGMENT COLOR RESEARCH REPORT

SUBJECT: CPC - Two-Stage Drowning Process Development

PERIOD COVERED: 6/1/69 to 3/1/70

SUBMITTED BY: W. L. Monson W. L. Monson Date Submitted: 4/28/70

APPROVED BY: W. A. West Date Issued: 5/7/70

ABSTRACT

An apparatus designed, constructed, and tested at Newport has demonstrated production, on a semi-works scale, of pigmentary CPC in the alpha-I form by a unique new process: Two-Stage Drowning. This report described the development of the process and the results of a study of factors controlling the quality of Two-Stage Drowned CPC.

TABLE OF CONTENTS

I. INTRODUCTION

The work reported here covers the demonstration of the production of pigmentary alpha-I phase CPC by a new process: Two-Stage Drowning, and an investigation of the factors controlling the quality of pigment so made. This study is a continuation of the development of the process for Acid Flushing - HT Drowning of CPC, first reported in KN-67-10.

Later work (to be covered in detail in a separate report by P. H. Griswold) had shown that ordinary (single-stage) drowning of BB-CPC (semichlor grade) yielded a mixture of CPC polymorphs; alpha-I and alpha-II, whereas the goal product, equivalent to N-623 (semi-finished acetone-milled BB-CPC), consisted of alpha-I. The alpha-II phase was shown to be unstable in paint grinds, converting to the more stable alpha-I form. This process of phase conversion is accompanied by acicular growth, leading to undesirable physical properties of the HT drowned pigment in paint (higher viscosity and worse flocculation than the acetone-milled product).

A thorough study by P. H. Griswold of phase equilibria in the system CPC-H_2SO_4-H_2O revealed the existence of several (possibly four) salts of CPC and H_2SO_4, each stable over a different range of H_2SO_4-H_2O concentrations. More importantly, he showed that the crystal form of the CPC recovered by hydrolysis of these various salts differed from salt to salt, and that pure alpha-I CPC could be recovered by hydrolyzing CPC·$4H_2SO_4$ (stable above about 66% H_2SO_4). As might be expected, the particle size of this CPC, recovered by hydrolysis of CPC·$4H_2SO_4$ formed by equilibration for substantial periods of time, was much too large for good pigment quality.

II. OBJECTIVE

It became the objective of this study to devise a practical method of forming and then hydrolyzing CPC·$4H_2SO_4$ to yield pigmentary alpha-I CPC, starting with "Flushed Acid" (CPC synthesis mass dissolved in 98% H_2SO_4). The most direct and obvious way to do so appeared to be "Two-Stage Drowning," as covered in the Discussion Section.

III. SUMMARY AND CONCLUSIONS

Pigmentary chlorine-free and semichlor CPC in the pure alphaI form can be produced easily by a continuous two-stage drowning of the acid layer from an "acid flushing" step following CPC synthesis. The slurry from the drowning

III. SUMMARY AND CONCLUSIONS (Cont'd)

operation (about 4% CPC in 35-40% $HPSO_4$) must be digested under suitable conditions to develop a sufficient degree of crystallinity to be a direct counterpart with respect to color strength, dispersibility, and rheology, of existing semi-finished product types such as N-623 (BBS), N-872 (BRA), and N-13 (BBX). Although some particle size growth takes place during this "development" step, the final size and masstone level are primarily determined in the drowning process; specifically, during first-stage mixing and retention between stages, when the CPC is precipitated from solution in 98% H_2SO_4, by dilution with a small amount of water, forming essentially pigmentary-sized particles of $CPC \cdot 4H_2SO_4$. Apparently, in the subsequent hydrolysis of this substance, during the second-stage mixing (dilution with remaining water), the resulting CPC retains the external morphology and size of the hydrosulfate particles from which it forms. CPC, isolated at this point, displays a low degree of crystallinity by x-ray diffraction. First-stage mixing factors shown to be controlling were mixer throughput rate (velocities at point of mixing), mass velocity ratio of diluent to acid, and composition and temperature of diluent (both pure water and 35% H_2SO_4 were tested as first-stage diluents). The important factors involved during interstage retention are time (controlled by length of pipe and flow rate), temperature (controlled by ingredient temperature and composition), and concentration (determined by ratio of diluent to acid).

Phase control was complete within the expected range of first-stage concentrations, in all but one of the 78 drownings covered here.

Separate reports by others will discuss work-up of two-stage drowned material for the BRA and BBX grades.

With respect to the utility of two-stage drowning of semichlor CPC to produce an N-623 (BBX counterpart, it was determined that:

a) Attainment of sufficient crystallinity requires use of an Arquad 16/Perclene treatment of the drowning slurry for several hours at 80°C.

b) The effect of degree of crystallinity on paint rheology differs markedly between paint vehicles. Nonsolvent treated two-stage BB is good in TAE-3 rheology but extremely poor in 30J.

III. SUMMARY AND CONCLUSIONS (Cont'd)

c) Increasing crystallinity by solvent treatment improved 30J rheology, but crystallinity equaling or even exceeding standard does not guarantee equal viscosity.

d) Increasing interstage retention time in drowning improves paint viscosity in all systems.

e) Standard 30J and TAE-3 rheology can be achieved simultaneously with standard color by solvent developing, to standard level of crystallinity, a material which has been held between stages for a sufficient length of time at a sufficiently high temperature. It has not been firmly established what factor is involved in the viscosity improvement but it is hypothesized that the probably greater perfection of crystallinity of the tetrahydrosulfate crystals before hydrolysis may play a role by producing a more perfect solid solution or less reactive CPC crystallite after solvent development.

f) Pure alpha-I BB-CPC as made by this process is metameric versus N-623, which contains a small amount of beta-phase CPC. The metamerism can be corrected by addition of beta-CPC, the exact amount needed depending on the chlorine content of the CPC.

g) The N-623 counterparts made by this new process require the same minimum Cl content (3.6%) as solvent milled material for adequate crystal stability in paint. Cl level also affects color properties of pigments made by both processes. Lower Cl leads to lighter, redder, duller, weaker and more crystalline products. However, the MT level and strength are easily corrected by varying two-stage drowning conditions, if desired.

h) There was no particular discernible effect of use of "high-concentration" BB-CPC synthesis slurry on either flushing or drowning, insofar as the resultant CPC quality was concerned. It is probable that the lower kerosene content of such slurry shouldbe beneficial in the flushing

III. SUMMARY AND CONCLUSIONS (Cont'd)

h) (Cont'd)

operation, but because of sampling difficulties from production synthesis kettles, the "high concentration" syntheses used were actually in the same range of kerosene contents as "normal concentration" material.

i) Acid/CPC ratios from 9/1 to 10/1 were used in various semi-works flushings. Little effect on resulting CPC quality could be noted from the data obtained. Any real effect was probably masked by the much larger quality effects of Cl level and drowning and development conditions.

j) The second-stage mixer was tested only in the form of a simple "Tee" mixer. Final H_2SO_4 concentrations between 35-40% (filtrate basis) were demonstrated to produce good quality, in conjunction with suitable flushed acid quality, first-stage conditions and suitable development.

k) The required first-stage mixer operating pressure drop is an important factor in scale-up and is the resultant of throughput rate, mass velocity ratio, and ratio of diluent to flushed acid. It was concluded that pressure drops in the range of 175-225 psi were required for production of suitable quality two-stage drowned material.

IV. PATENT SITUATION

The principle of two-stage drowning as applied to production of pigmentary CPC of desired phase (and perhaps also to production of QA and other colors) may be patentable. The patent status of the use of a "Bullet Mixer" in conjunction with Two-Stage Drowning is discussed in a letter from R. D. Nutting to R. H. Wetzel, shown in the Appendix.

V. RECOMMENDATIONS FOR FUTURE WORK

It seems likely that the general principle of producing controlled polymorphic forms of pigments which are stable and protonatable in acid solution by a Two-Stage Drowning procedure, as described here for CPC,

V. RECOMMENDATIONS FOR FUTURE WORK (Cont'd)

could be extended to quinacridones and other pigments which are salt-forming. The salt formed need not necessarily simply be that produced by solvation. For example, it is possible that the beta-QA produced by drowning an H_2SO_4 solution of QA containing PTSA is formed by hydrolysis of a QA-PTSA salt, or mixed salt with QA-H_2SO_4. Further work with CPC itself could prove fruitful, for example, to demonstrate production of pure alpha-II CPC by hydrolysis of CPC·$2H_2SO_4$ (possibly a useful starting material for conversion to beta-CPC). It is even conceivable that the correct type of salt could hydrolyze directly to beta-phase CPC.

The necessary prelude to commercial exploitation of such possibilities is a knowledge of the phase equilibria in suitable selected three, four, and higher component systems and the determination of whatever specificity may exist in conversion to the various polymorphic forms of the pigments by hydrolysis of solid salts produced.

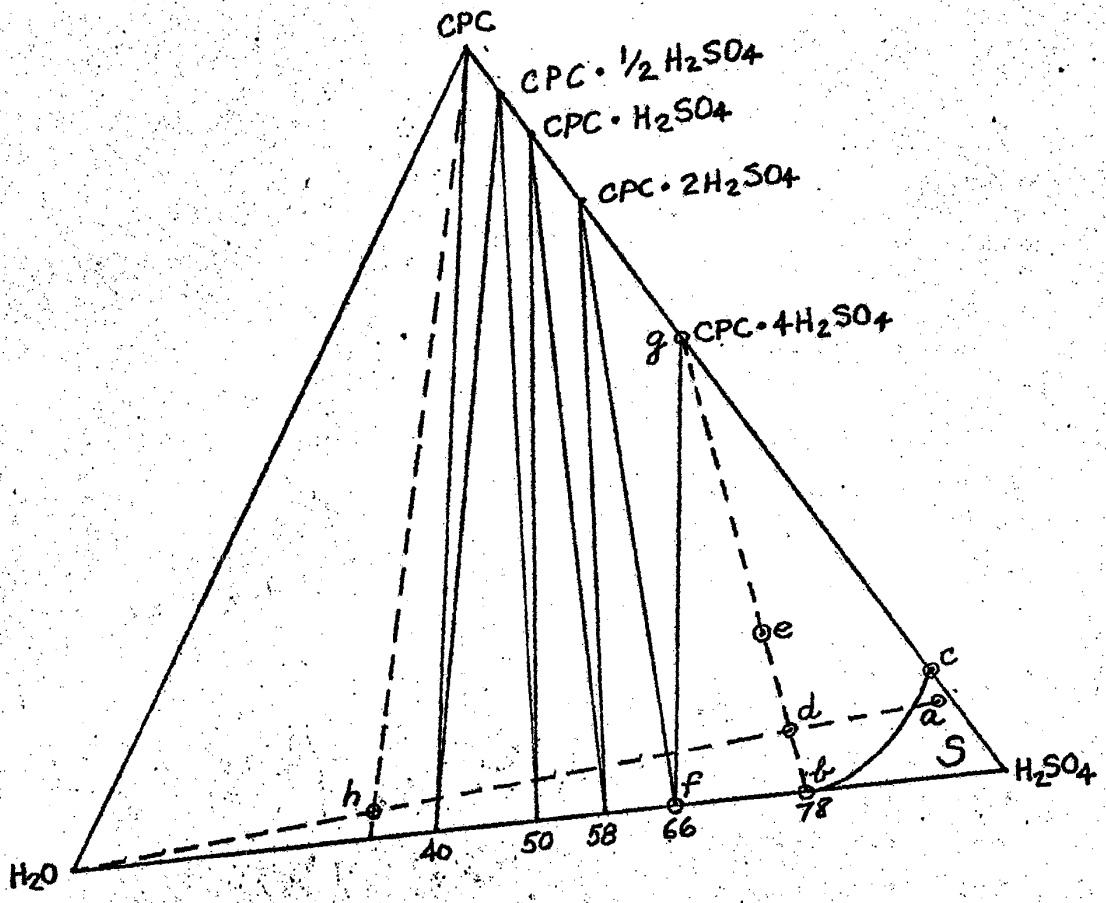
VI. DISCUSSION

A. Phase Equilibria

The principle of two-stage drowning is best understood by reference to the phase diagram for the three-component system CPC-H_2SO_4-H_2O, as shown on the next page. This diagram was established by P. H. Griswold, using purified CPC, sulfuric acid, and water. It should be understood that in the "Acid Flushing" and drowning process one is actually dealing not with a simple three component, but a much more complex, system.

This is because in the process of dissolving CPC in 98% H_2SO_4 during the flushing step, there are also dissolved all other components in the synthesis mass, except kerosene. The exact composition of this mixture is not fully known, but it certainly includes decomposition products of excess urea, such as cyanuric acid; unreacted ingredients; by-products, such as phthalimide; and kerosene sulfonic acids. It is known that these other components are present to the extent of some 60-75% of the weight of the CPC itself. In order to simplify the analysis of phase equilibria, it is convenient

THE TERNARY SYSTEM $CPC - H_2SO_4 - H_2O$



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VI. DISCUSSION (Cont'd)

A. Phase Equilibria (Cont'd)

(but of course not strictly correct thermodynamically) to lump together all the other substances present as a "fourth component". We can then consider that we are dealing with a plane section of the four-component isotherm (a tetrahedron) cut at a slight angle to the CPC-H_2SO_4-H_2O plane, passing through the H_2O vertex and the composition of the "flushed acid". The phase boundaries of such a section will be distorted as compared to the simple three-component system, but as long as entirely new "four" component phases do not appear, it seems valid to determine and allow for possible phase boundary shifts experimentally and keep the simplicity of the three-component diagram. A somewhat different approach is to treat the "fourth component" as though it were water. In view of the experimental result that the critical phase boundary (fg in diagram) in the region of most interest is not significantly altered when using this approximation, it appears a practical and useful simplification. Of course the enthalpy, and therefore, the heat of dilution (and adiabatic temperature rise) of flushed acid is significantly higher than that of a three-component composition of the same % CPC and % H_2SO_4.

Referring to the three-component phase diagram, there is only one single-phase three-component region in the entire system. It is labeled "S", and is bounded by the H_2SO_4-H_2O axis from about 78-100% H_2SO_4, the CPC-H_2SO_4 axis from 0 - about 12% CPC, and the solubility curve for CPC. Inside "S" there exists a single homogeneous liquid phase. The composition of "Flushed Acid" falls inside the region of complete solubility. A typical composition for BB-CPC might be 9% CPC, 81% H_2SO_4, 1.6% H_2O and 8.4% "fourth" component.* On mixing such a solution with water, the total composition must always fall along the straight line connecting point "a" with the H_2O vertex. On adding water slowly to the acid/CPC solution the first

*The projection of this onto the three component plane falls at point "a", inside S.

VI. DISCUSSION (Cont'd)

A. Phase Equilibria (Cont'd)

appearance of a new phase is when the solubility curve "bc" is reached. At this point a precipitate having the composition $CPC \cdot 4H_2SO_4$ begins to form. As more water is added the proportion of CPC precipitated in the form of this salt increases until at point "d" virtually all the CPC is in the solid phase. If this two-phase mixture is filtered, it is possible to separate a liquid having the composition "b", the resulting filter cake having the composition "e". By the Phase Rule principle known as the "Law of the Straight Combining Line", a straight line extended from point "b" through point "e" will intercept the composition of the solid phase. This technique was used to identify the solid phase composition in equilibrium with various H_2SO_4-H_2O compositions when preparing the original phase diagram. By this means it was shown that above 66% H_2SO_4 the equilibrium solid phase is $CPC \cdot 4H_2SO_4$. From about 58 to 66% H_2SO_4 the equilibrium solid phase is $CPC \cdot 2H_2SO_4$. Above about 78% H_2SO_4, there is appreciable solubility of the CPC. In order to precipitate all the CPC as the tetrahydrosulfate, then, enough water must be added to give a resultant liquid phase composition of 66-78% H_2SO_4. This mixture must then be allowed to equilibrate a sufficient length of time to ensure elimination of any localized regions of high or low concentration and to perfect the crystallinity of the precipitate. These processes are, based on experimental results, accompanied by growth of the crystals, and their rates are functions of the time held, temperature, and concentration. Once having been formed and equilibrated, the precipitate of $CPC \cdot 4H_2SO_4$ can be hydrolyzed rapidly and completely by addition of enough water to drop the liquid phase composition to a value below about 40% H_2SO_4, for example, point "h" in the diagram. Below this concentration the only stable solid phase is CPC itself. Since the salt being hydrolyzed is pure $CPC \cdot 4H_2SO_4$, the resulting form of CPC is the desired pure alpha-I.

Initially it was uncertain that sufficient phase purity could be achieved in pigmentary sized CPC, since the required equilibration of the tetrahydrosulfate is accompanied by growth. The external morphology of hydrosulfate crystals has been shown by A. R. Hanke to be maintained on hydrolysis. In fact, it was quickly demonstrated that pigmentary

VI. DISCUSSION (Cont'd)

A. Phase Equilibria (Cont'd)

alpha-I CPC could be produced by careful control of mixing and equilibration conditions.

B. Two-Stage Drowning Apparatus

A schematic drawing of the apparatus designed and constructed at Newport to study two-stage drowning is given in the Appendix. The apparatus consists of the following elements.

1. A nitrogen pressurization and flow measuring system.

2. Blowcases for flushed acid and the first stage diluent.

3. Shut-off (ball) and control (needle) valves for acid and first stage diluent.

4. First stage mixer, pressure gauges, and check valves.

5. Interstage holdup loops (various lengths to give various retention times).

6. Second stage mixer, in which the mixture from the interstage holdup loop is mixed with the balance of the water to give the final desired composition. Second stage water is pumped from a 20-gallon supply tank by a Jabsco centrifugal pump.

7. Product collection system permitting sampling of both first and second stage.

The unit was designed to operate in a range of throughputs up to about 1/2 scale of the proposed plant installation.

Sketches of the initially used first and second stage Tee mixers are shown in the Appendix. After the first few runs, various types of Bullet mixers were substituted for the Tee mixer in the first stage and were used in the balance of the work reported here. A sketch of one of these versions, used in most of the runs, is also shown in the Appendix.

VI. DISCUSSION (Cont'd)

C. Experimental Runs

1. General Procedure

During the period covered in this report, 78 drowning runs were made. A number of these were made from chlorine-free CPC for work-up into N-872 (BRA) counterparts, several runs were made from BB-CPC for work-up into N-13 (BBX), and a few others were made from both types of CPC for filtration tests by the Expansion Task Force. The remainder, to be discussed here, were made from BB-CPC, to be worked up as candidate N-623 (BBS) counterparts.

To obtain satisfactory pigment quality with respect to tinting strength, dispersibility, and paint viscosity, it is necessary to develop the drowned BB-CPC and the experimental work reported here covers both drowning and development variables.

In general, "as drowned" BB-CPC is too poorly crystalline to distinguish clearly between modifications of the alpha form. This is true whether it is single or two-stage drowned. Only by a post-drowning development step is a sufficient degree of crystallinity obtained to make a clear distinction. The development step consists of treatment of the drowned slurry with a suitable solvent and surfactant, as described by P. H. Griswold in KN-67-10. The development step can then be said to "reveal" the type of crystallographic modification inherently present in the "as drowned" material. There are two significant exceptions to this:

a. Sufficient equilibration of the BB-CPC tetrahydrosulfate (for example, holding overnight at 100°C) and subsequent hydrolysis without development can give a fairly crystalline product distinguishable as alpha-I CPC. Of course, this material is not of pigmentary size.

b. Chlorine-free CPC is much more mobile with respect to crystallographic transformation and will convert quickly to fairly crystalline pure alpha-I in hot "as drowned" slurry (about 30-40% H_2SO_4) even when single-stage drowned, without use of solvent in development.

VI. DISCUSSION (Cont'd)

C. Experimental Runs (Cont'd)

1. General Procedure (Cont'd)

It should be borne in mind that no practical amount of "development" will completely transform the mixture of alpha-I and alpha-II forms of CPC obtained by single-stage drowning to pigmentary, crystalline, pure alpha-I BB-CPC. It follows that, when pure alpha-I phase is obtained after two-stage drowning and development of BB-CPC, the hydrolysis product must have been inherently of that modification, even though of a low degree of crystallinity.

In general, the as-drowned product from a "TSD" (Two-Stage Drowning) run was subjected to more than one development condition, a number of which semi-finished products were then finished by suitably modified Newark processes into BT-284-D, BT-425-D, etc., and evaluated by a variety of physical and end-use tests, including:

Rubout

Paint Tests (Alkyd and acrylic enamels, acrylic lacquer by ball and sand milling for hue, tinting strength, dispersibility, flocculation, viscosity)

Ink Mill Tests (Lithographic tests)

Specific Surface

Electron Microscopy

Fluid Ink

X-Ray Diffraction (Phase, crystallinity)

For convenience, the complete data are tabulated in Section VII.

VI. DISCUSSION (Cont'd)

C. 1. General Procedure (Cont'd)

The general plan of experimental attack was as indicated below:

a. Make a few initial runs to establish that phase control was being reliably achieved in a pigmentary product; the primary aim of the work.

b. Undertake a study of drowning conditions to establish their effects on resultant pigment quality, other than phase.

c. Use this information to define conditions needed to produce goal quality BB-CPC by Two-Stage Drowning and demonstrate production of that quality in amounts sufficient for thorough evaluation.

2. Results

a. Demonstration of Phase Control

Drowning and development conditions for TSD-1 are described in the Experimental Data, Sec. VII. The product examined as an N-623 by rubout and x-ray, then worked up into BT-284-D and tested in 30J, TAE-3, and 927 lacquer paints. The quality of this material was very encouraging for several reasons:

(1) Rubout color reasonably close to N-623. Basically pigmentary.

(2) X-ray diffraction pattern showed good crystallinity with no indication of presence of alpha-II.

(3) Paint results were reasonably good:

(a) Equal flocculation.
(b) Slightly red tint.
(c) Slightly light masstone.
(d) Equal or better viscosity in TAE-3 and 927 lacquer.
(e) Slightly worse viscosity in 30J.

VI. DISCUSSION (Cont'd)

C. Experimental Runs (Cont'd)

2. Results (Cont'd)

a. Demonstration of Phase Control (Cont'd)

Overall, this type of quality exceeded that made by single-stage drowning. The most important result was that pigmentary size BB-CPC had been made in the desired pure alpha-I form by an acid pasting-HT drowning route; as far as is known for the first time. Electron micrographs* and specific surface indicated that pigment size was slightly larger than standard BT-284-D. At the time this was thought to be responsible for the redness of tint and lighter masstone. The slightly worse viscosity in 30J was disappointing (particularly for a larger rather than smaller particle size material) since it had been expected to be good, in line with high alpha-I phase purity. However, paint viscosity is also partly determined by development conditions and it was felt that 30J viscosity could be improved by an appropriate adjustment of development.

In the second, third, and fourth runs (all made using the Tee mixer first stage), minor changes in drowning conditions and variations in solvent development were directed toward production of slightly smaller particle size material to give the desired darker masstone vs. N-623, while retaining alpha-I phase purity and the desirable properties obtained from working up TSD-1.

The following briefly summarizes summarizes pertinent results of these four runs:

(Table on next page)

*See Appendix.

VI. DISCUSSION (Cont'd)

C. 2. a. Demonstration of Phase Control (Cont'd)

TSD Run No.	Drowning Variable	Development Variable	Rubout vs.N-623 MT	Rubout vs.N-623 T.S.	Spec. Surf.	27° V.P.	Phase	6 RPM* Brookfield 30J	6 RPM* Brookfield TAE-3
1	Control	Control	Lt_{12}	104	66	56	α-I	1.18	0.83
2	No Change	Use 160% Perclene in place of 100% ODCB	Lt_{12}	104	61	51	α-I	1.20	--
		No solvent	Lt_{12}	115	24	0		2.40	--
3	Reduce first stage conc. from 71.8 to 68.6% H_2SO_4	Use 100% Perclene	Lt_{12}	106	67	44	α-I	2.13	--
		No solvent	Lt_6	110	20	0		3.00	--
4	Like 3, but also reduce first stage retention from .037 to .026 sec.	Use 100% Perclene	Lt_{12}	105	69	43	α-I	1.67	--
		No solvent	Lt_3	115	37	0		--	--

*Ratio of sample viscosity to that of Standard BT-284-D.

The results from this set of runs showed that alpha-I phase was being consistently produced, and that little change in MT level had been achieved except when solvent was entirely eliminated. However, this nonsolvent treated material was quite low in specific surface (indicating aggregation) and in degree of crystallinity (indicated by 27° Valley Parameter), resulting in poor dispersibility, tinting strength, and viscosity.

VI. DISCUSSION (Cont'd)

C. 2. a. Demonstration of Phase Control (Cont'd)

It had been hoped that the two-stage drowning procedure might eliminate the need for use of solvent development, but this series (and subsequent series of runs) confirmed that adequate dispersibility, and particularly 30J paint viscosity, required the high degree of crystallinity which only solvent treatment is known to impart.

b. Variable Study

The general effect and relative importance of the variables are summarized in the tabulation below, and then discussed in more detail in the rest of this section.

Most Important Variables	Effect
% Cl in BB-CPC	Lower Cl results in lighter, duller, redder, weaker products. Need at least 3.6% for adequate crystal stability.
First-Stage Mixing Conditions	Control base particle size and MT depth of product.
Interstage Retention Conditions	Partly control base particle size. Strongly affects paint viscosity independently of size. Some minimum condition essential for phase control.
Development Conditions	Imparts crystallinity needed for Good dispersibility and paint viscosity. Lightens MT.
Variables of Lesser Importance	**Effect**
Second-Stage Mixing Conditions	Little observed effect by variation of final concentration from 21% to 37% H_2SO_4.
Ratio of Acid/CPC in Flushing	In range of 9/1 to 10/1, little or no observed effect on final CPC quality.
BB-CPC Synthesis Concentration	No observed effect. Possibly masked by other variables.

VI. DISCUSSION (Cont'd)

2. b. Variable Study (Cont'd)

(1) The Cl levels of the BB-CPC used in this work were as shown:

TSD Runs	% Cl	Synthesis Conc.
1-18	4.0	Normal
19-56	3.4	High
57-68	3.6	High
69-78	4.0	Mixed

The specification range of % Cl for acetone-milled BB is 3.6-4.5%. It had been planned to make a systematic study of the effect of Cl contents, within the specification range, on quality of two-stage drowned CPC. Unfortunately, this plan could not be carried out, since it was thought to be more urgent to test the combined effect of high BB synthesis concentration (as planned for the proposed CPC expansion) and two-stage drowning. This meant that the number of syntheses from which starting material could be selected was restricted to the few made at high concentration. As it happened, these were below specification Cl levels, and far enough below to seriously affect color, as well as crystal stability (just as in the acetone milling process).

After eleven runs had been made with the 2.6% Cl material (Runs TSD-57 to TSD-68) which could not be worked up to a satisfactory tinctorial match with N-623 in paint and which also were seriously deficient in crystal stability, it was agreed to abandon use of "High-Concentration" slurry and return to starting material of 4.0% Cl. All the spec. material had same Cl content. Consequently, the exact effect of small variations in Cl content within the specification range could not be determined experimentally. It can reasonably be inferred to be like the effect on quality of acetone-milled BB.

VI. DISCUSSION (Cont'd)

C. 2. Results (Cont'd)

b. (2) First-Stage Mixing

A modified "Bullet" mixer (adapted from a DuPont ESD design) was constructed and used (in three versions) from Runs 5 through 78 as a replacement for the "Tee" mixer used in the first four runs. The decision to change to this type of mixer was based on several considerations:

(a) Reported easier scale-up to plant size.

(b) The increasing recognition that first-stage mixing conditions were among the most important factors in two-stage drowning.

(c) Greater flexibility in altering mixer geometry, thus affecting flow conditions at the point of mixing relatively easily to suit process requirements.

Detail drawings of this mixer are shown in Section VIII - Appendix. The acid nozzle shown (Part "B") is the eight-hole model. Four, eight, and sixteen hole nozzles were constructed and tested. The total cross-sectional area for acid flow was held constant in this set of nozzles.

With this type of mixer, throughput rate (which determines velocity and Reynolds number at the point of mixing), diluent composition, and mass velocity ratio of water to acid (approximate decreasing order of effect) were found to be critical in determining the base particle size of the resulting pigment.

VI. DISCUSSION (Cont'd)

C. 2. Results (Cont'd)

b. (2) First-Stage Mixing (Cont'd)

Combined Effect of Varying Bullet Mixer Flow Rate and Interstage Retention

BII Mixer

% Cl: 2.6, Standard Development Conditions
Diluent Composition: H_2O
Mass Velocity Ratio: 1.0
Interstage: Temp. 108-110°C,
Conc. 71.5-73.8% H_2SO_4,
57" x 1" Pipe

TSD No.	Rotameter Readings Acid	Water	Interstage Retention Sec.	% Perclene Devel.	R/O vs. N-623	Relative - 30J Brookfield 6 RPM
61	32	35	3.3	100	Lt_{25} 100 RD	1.54
				200	Lt_{25} 100 RD	-
62	40	44	2.7	100	Lt_{12} 100 RD	1.4
				200	Lt_{12} 100 RD	1.8
63	50	55	2.3	100	Eq. 97 vsRD	2.0
				200	Eq. 97 vsRD	1.7

Effect of Mass Velocity Ratio*

BII Mixer

% Cl: 2.6, Standard Development Conditions,
Diluent Comp.: H_2O
Interstage: 57" x 1" Pipe

TSD No.	M.V. Ratio W/A	Rotameter Readings Acid	H_2O	Clearance Mils	Interstage $\%H_2SO_4$	Temp. °C	Time Sec.	R/O vs. N-623
51	0.23	60	66	35	-	101	1.9	Lt_{99} 106 RD
52	0.53	60	66	15	74.4	96	1.9	Lt_{20} 100 RD
60	0.8	32	35	10	72.7	108	3.5	Lt_{35} 100 RD
61	1.0	32	35	8	71.5	109	3.5	Lt_{25} 100 RD

*Mass Velocity Ratio = $\frac{\text{(Water Vel. x Sp.Gr.)}}{\text{Acid Vel. x Sp. gr.)}}$ at mixing point, which is at acid hole circle in clearance.

VI. DISCUSSION (Cont'd)

C. 2. Results (Cont'd)

b. (2) First-Stage Mixing (Cont'd)

Effect of First-Stage Diluent Composition

BII Mixer

TSD No.	First Stage Diluent	Rotameter Readings Acid	Rotameter Readings Dil.	Mixer Clearance, Mils	M.V. Ratio	Ret. Time, Sec.	R/O vs. N-623	Spec. Surf. $M^2/g.$
19	H_2O	60	100	10	1.2	0.4	Lt12 99	73
20	35%H_2SO_4	31	100	35	1.0	0.6	E 100	87
						BT-284-D	Std.	70
					Ave.	35% H_2SO_4	Dil'n	83
					Ave.	H_2O	Dil'n	74

(3) Interstage Retention

Interstage retention conditions were found to strongly affect resultant paint viscosity, as well as having effects on MT level. The effect on paint viscosity was not simply due to CPC particle size, (as measured by MT level) or degree of crystallinity (as measured by X-ray diffraction). Final products with the same MT color and 27°V.P. were substantially different in 30J viscosity depending on interstage temperature, time, and concentration (approximate order of decreasing effect). It is hypothesized that one effect of retention is to perfect the crystallinity of the tetrahydrosulfate which might result in CPC of improved morphology, degree of solid solution, or reactivity. Particle size growth of the tetrahydrosulfate also must take place, judging by the effects on resultant CPC size. Techniques are not yet known for measurement of transient crystallinity and particle size of the tetrahydrosulfate, so no direct physical tests could be made.

VI. DISCUSSION (Cont'd)

C. 2. Results (Cont'd)

b. (3) Interstage Retention (Cont'd)

The following series of runs illustrates the effects described:

Interstage Retention Conditions vs. Quality

TSD No.	Interstage Temp. °C	Interstage Time Sec.	Interstage Conc. %H_2SO_4	27° V.P.	R/O vs. N-623	30J Rel.Visc. Brookfield 6RPM	Brookfield 60RPM	Ford Cup	Spec. Surf. M^2/g.
8	110*	0.026	66.9	43	Dk_2	2.29	1.90	1.52	73
9	110*	0.124	68.7	42	Lt_2	1.15	1.34	1.13	66
13	110*	0.814	69.2	44	Lt_{12} 95	1.07	1.07	0.95	78
14	110*	0.287	70.7	33	Lt_6 100	1.60	1.45	1.15	-
15	110*	0.071	70.0	29	Lt_6 102	2.40	2.00	1.70	77
65	105	5.5	73.6	62	Dk_2 100 RD				
67	122	5.5	72.9	62	Lt_6 98 RD				
68	134	5.5	72.4	61	Lt_{99} 102 RD				
70	118	5.5	72.3	51	Lt_{29} 104 RD	1.00	1.10	1.00	-
71	102	5.5	73.0	53	Lt_6 106 RD	1.82	1.41	1.34	-

*Estimated.

(4) Development Conditions

Development conditions were adapted from those used on single-stage drowned BB, as reported in KN-67-10. For the most part, they involved the use of 5% Arquad 16 (based on pigment weight) and 0-200% Perclene or ODCB. A cationic agent like Arquad is needed to effectively disperse pigment and emulsify solvent in the hot 35-40% H_2SO_4 - containing drowned pigment slurry. Most of the Arquad is retained by the pigment and improves its dispersibility markedly. Since the Arquad is a diluent, the purity of the N-623 equivalent is lower than non-surfactant treated material (about 92%, vs. 96% CPC for N-623). This was compensated for when extending with CaSx, so as to arrive at the same CPC content as BT-284-D, 88%.

VI. DISCUSSION (Cont'd)

C.2.b. (4) Development Conditions (Cont'd)

Data shown below illustrate the effect of the type and quantity of solvent and the time and temperature of solvent treatment:

Quality vs. Development Conditions

TSD No.	% Arq.	Type Solvent	% Sol. vent	Time Hr.	Temp. °C.	R/O vs. N-623	27° V.P.	Sp. Surf.	Ratio of Viscosities Sample/BT-284-D 6	60	FC	6	60	FC
10	5	None Used	0	1	80	Dk_4 115	0	42	4.25	2.54	2.44	.92	.98	.82
		Perclene	33			Lt_8 101	34	65	2.33	1.57	1.29	1.21	1.15	.94
			66			Lt_8 100	42	70	2.33	1.51	1.29	1.21	1:11	.96
			100			Lt_8 98	44	70	2.33	1.49	1.22	1.13	1.13	.92
12	5	None Used	0	1	80	Dk_{12}115	0	54	2.19	1.86	1.72	1.04	.98	.85
		Perclene	100			Lt_{10} 97	47	74	1.43	1.36	1.19	1.21	1.18	.98
		"	200			Lt_{10} 97	53	76	1.00	1.04	0.86	1.21	1.16	.97
		ODCB	100			Lt 97	60	77	1.00	1.04	0.86	1.13	1.10	.93
63	5	Perclene	100	2	80	Lt_{12}105 G4 I4	64	-	1.4	1.36	1.21	.85	.96	.98
	5	"	100	2	45	Lt_{10}103 G4 I4	64	-	1.3	1.29	1.18	.85	.96	.93
65	5	Perclene	100	1	80	Lt_9 103 G	62	-						
				4		Lt_{10}107 G D_4	64	-						
				7		Lt_{12}107 G D_4	63	-						
35	0	ODCB	100	1	80	Dk_{99}150	55							
	2	"	"	"	"	Lt_{10}102	56							
	5	"	"	"	"	Lt_8 104	56							

VI. DISCUSSION (Cont'd)

C.2.b. (4) Development Conditions (Cont'd)

Several experiments were run in attempts to increase MT depth by using Arquad in the first stage drowning water, using an Arquad/Perclene emulsion in the second stage drowning water and by application of shear (in a Waring Blendor) to the drowned slurry before development. None of these was effective.

During this work it was found that the redness of tint of the products being made was excessive vs. N-623, particularly with the low % Cl material and with more severe development. However, even with high Cl and the minimum development needed, products were generally redder than desired. Eventually it was recognized that the redness was partly associated with metamerism and that this was due to absence of any beta-phase in the drowned, developed material. Addition of beta, either by blending or seeding corrected both redness and metamerism. Only a small amount is needed, with good Cl levels.

(5) Second-Stage Mixing

Second-stage mixing throughout this series of runs was tested only in a Tee mixer, designed to have the mass velocity ratio of the side-entering stream (the first-stage mixture) to that of the second stage water be about 1.8. The velocity of the mixture was designed to be in the range of ordinary single-stage HT tubes. The only variables in the series were throughput rate and mixture ratio (which determines final mixture $\%H_2SO_4$ and %CPC). For chemical and economic reasons, it is desirable to approach but not exceed a final drowned $\%H_2SO_4$ of about 40% (filtrate basis) as closely as possible. Final concentrations of 21 to 37% H_2SO_4 were reached in this series. There was no evident quality incentive to drown to concentrations below 36%, based on the limited data available.

VI. DISCUSSION (Cont'd)

C.2.b. (6) Ratio of H_2SO_4/CPC

The bulk of the flushed acid used in this work was nominally 9/1. It was found that at this level, crystallization would take place at an undetermined point somewhere below normal room temperature. Several batches of acid had to be discarded after outdoor exposure in winter. To conserve material, the ratio of acid/CPC was increased to 10/1. Any real quality effect of this change was small or else masked by larger effects due to Cl level, etc.

(7) BB-CPC Synthesis Concentration

In conjunction with the proposed CPC expansion, BB synthesis concentration is planned to be increased. All of the "high concentration" BB slurry used in this work was unfortunately also low in % Cl. Consequently no clear-cut comparison of final effect of high vs. normal concentration could be made, since % Cl and other important quality factors were also varied simultaneously.

c. Combination of Optimum Conditions

The best drowning and development conditions known at the time were used on flushed acid made from 4.0%Cl BB in Run TSD-78 in an attempt to demonstrate production of completely satisfactory material. When extended with CaSx to 88% CPC, it compared favorably in ink and paint vs. BT-284-D with respect to color, crystal stability, flocculation and viscosity (both 30J and TAE-3 paints.) The following table summarizes test results of this product.

TSD-78 - Drowning Conditions

Date Drowned: 2/19/70, Acid Lot: 00013, %Cl: 4.0
Mixer: BII(8 hole), 8 mils clearance, Acid Flow 4.3 GPM
Acid Temp.: 22°C, 1st St. Water Flow 1.6 GPM, Temp. 59°C.
Pressure at Mixer Inlet: Acid 200 psi, Water 180 psi.
Interstage Conditions: 57" Length 1" pipe, 2.2 sec. retention, 118°C mixture temp., 73.2% H_2SO_4 first stage filtrate.
Second Stage: 10.6 GPM water flow, mixture temp. 79°C, 36.5% H_2SO_4 filtrate.

VI. DISCUSSION (Cont'd)

C.2.c. Combination of Optimum Conditions (Cont'd)

Development and Evaluation as N-623

NB #1860 - 130A, B, C, D, E, F
5% Arquad 16, 2 Hr., 80°C

Sample	% Per-clene	% CPC	Valley Parameter 27°	Valley Parameter 15°	% beta by X-ray Diff.	Sp. Surf.	Remarks	R/O vs. N-623
A	100	91.4	45	41	0	69	No beta added	Lt_6 100 R D
B	100	-	43	43	5	70	2% BGS add.	Lt_8 103 R D
C	200	91.1	52	45	4	74	"	Lt_{10} 102 R D
D	100	-	49	45	7	76	4% BGS add.	Lt_8 103 sR sD
E	100	91.1	51	49	5	81	Seeded: 1/4% N-797	Lt_8 104 sR sD
F	100	-	48	50	10	73	Seeded: 1/2% N-797	Lt_9 105 sG sD

Laked with CaSx and Evaluated as BT-284-D

NB #1897 - 4A, B, C, D, E, F

Sample	R/O vs. BT-284-D	30J Brookfield 6	12	30	60	Ford Cup Sec.	TAE-3 Brookfield 6	12	30	60	Ford Cup Sec.
A	Dk_2 96 vsR vsD	6	8	11	16	39	12	14.5	20	25.5	57
B	Dk_2 95 vsR	5	7.5	10.5	14.5	38	10	12	16.5	22.5	52
C	Dk_4 96 vsR vsD	7	8.5	12	17	41	11	14	18.5	25	55
D	Dk_2 95 vsG vsI	5	7.5	10.5	15	39	10	12.5	16.5	22	50
E	E 96 vsG vsI	5.5	7.5	10.5	15	39	10	13	17	23	53
F	Lt_2 97 vsG vsI	5	7	10	14	39	11	13	17	22.5	54
BT-284-D, PS98090		5.5	8	11	15.5	45	10.5	13.5	17.5	23.5	58

VI. DISCUSSION (Cont'd)

C.2.c. Combination of Optimum Conditions (Cont'd)

Note that the translation of rubout color from N-623 to BT-284-D involves a shift in relative MT level. For example, Sample A, which is Lt6 vs. N-623 is Dk2 vs. BT-284-D. This does not involve any change in the sample on laking, but is merely due to the fact that the current N-623 in-process standard is darker than that from which the BT-284-D standard was made.

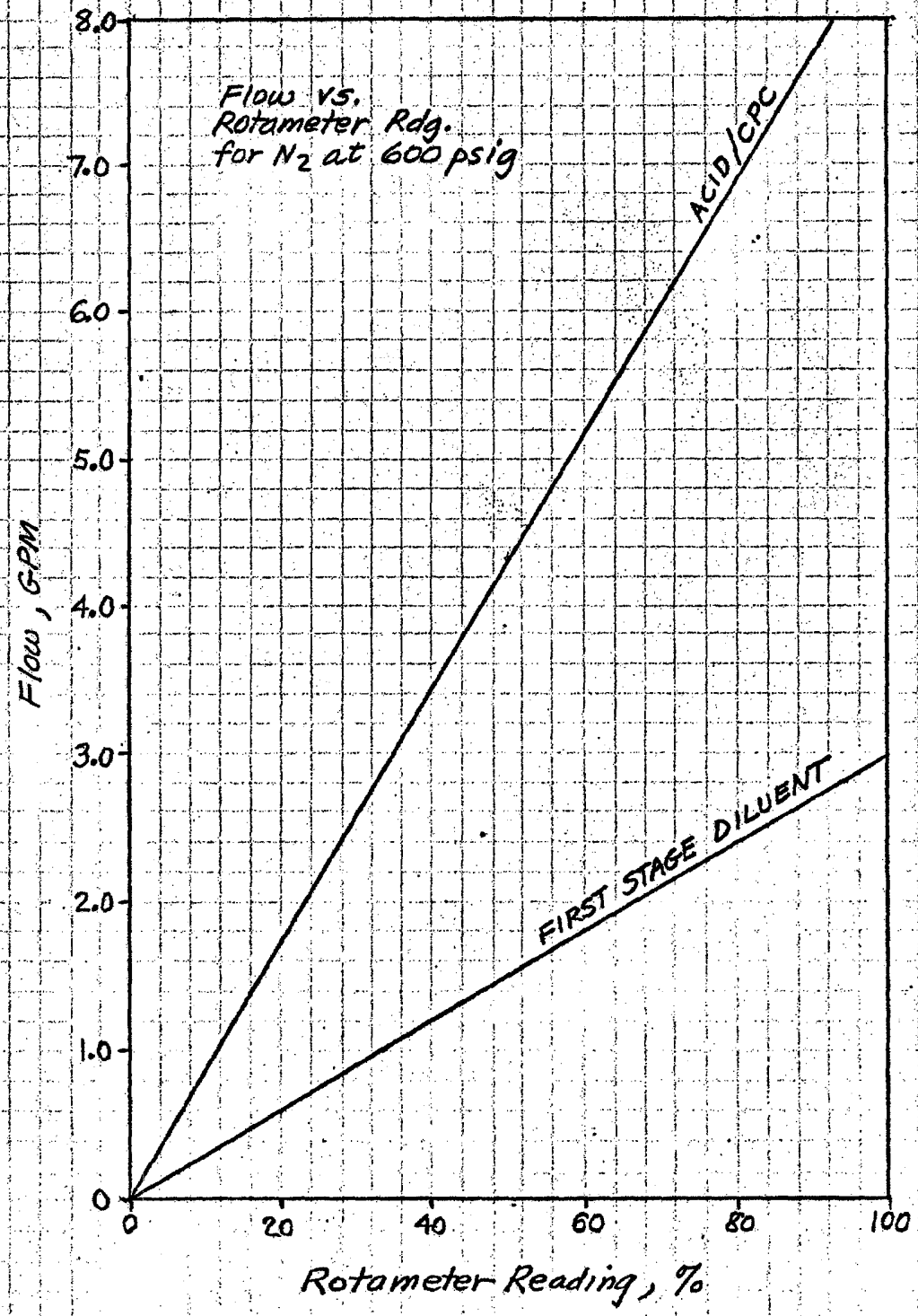
X-ray diffraction patterns for Samples A and E are shown in the Appendix, Sec. VIII.

VII. EXPERIMENTAL DATA

VII. EXPERIMENTAL DATA

The drowning and development data and pertinent evaluation results are tabulated, for runs TSD 1-77, on the next fourteen pages. Complete data for run TSD-78 are given in Section VI. C. 2., Discussion of Results of Experimental Runs.

In general, the headings are self-explanatory. Under "Mixer", BI, BII, and BIII indicate 4, 8, and 16 hole acid nozzle designs respectively. First stage diluent and acid flows are in percent of full scale Rotameter readings. A calibration is shown on the next page. Where indicated, first-stage diluent and acid temperatures are given in the Flow column. Where not shown, temperatures were ambient. Up through run TSD-42, first and second stage mixture temperatures shown are dial thermometer readings. These are mainly inaccurate, reading much too low because of insufficient running time, and thermometer lag. After TSD-42 readings are accurate and measured on samples taken out of the system. The "Clearance" shown in the "Mixer" column is the gap, in mils, between the acid nozzle and the impingement plate. This, with flow rate, determines water velocity at the mixing point.



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BB

			FIRST STAGE								INTER-STAGE		SECOND STAGE					DEVEL. PROD.							
TSD ±	ACID LOT	%Cl	MIXER	ACID FLOW	DIL. FLOW	D/C RATIO	PRESS.	TEMP. OUT	ACID CONC.	LGTH/DIL	TIME SEC.	VEL. FPS	H_2O FLOW	ACID CONC.	TEMP. OUT	% CPC	NB #	% ARO.	SOLV. QTY/TYPE	TEMP.	% CPC	27° VP	76° VP	PHASE	SPEC. SURF.
1	447-1	4.01	Tee	61	78	0	260	85	71.7	10/277	.037	38.2	20	25.4	80	—	92A	5	100/0	80/1	90.7	56	50	1.47	66
2	"	"	"	60	76	"	265	76	71.8	10/277	"	38.2	"	26.2	70	93.7	94A	"	160/P	"	89.8	51	49	1.56	61
																	B	"	0	"	89.7	0	0		24
3	"	"	"	60	101	"	425	65	68.6	10/277	"	41.9	"	24.8	60	94.6	98A	"	100/P	"	89.7	44	41	1.52	67
																	B	"	0	"	89.6	0	0		20
4	"	"	"	60	100	"	350	85	69.2	5/277	.026	41.9	"	26.2		93.6	100A	"	100/P	"	89.5	43	42	1.66	69
																	B	"	0	"	90.4	0	0		37
6	447-½	"	B I	58	100	"	85	77	68.0	5/277	"	41.9	"	26.0	70		106A	"	100/P	"	91.5	41	44	1.78	74
																	B	"	0	"	91.0	0	0		
7	"	"	B II	60	(36)	"	430	77	77.7	5/277	"		"	28.6	72	93.4	110A	"	100/P	"	92.0	44	42	1.60	
																	B	"	0	"	91.1	0	0		59
8	"	"	"	60	100	"	480	79	66.9	5/277	"	41.9	"	26.2	72	93.1	114A	"	100/P	"	91.3	43	37	1.63	73
																	B	"	0	"	90.5	0	0		7
9	422-½	4.30	"	60	100	"	420	30	68.7	50/277	.124	41.9	"	26.4	50	92.7	118A	"	100/P	"	90.8	42	38	1.72	66
																	B	"	0	"	89.6	0	0		37
10	448-1	4.01	"	59	100	"	520	35	70.3	50/277	.124	41.9	"	26.2	55	94.0	122A	"	100/P	"	91.0	44	44	1.57	70
																	B	"	0	"	90.5	0	0	—	42
																	C	"	33/P	"	91.2	34	42	1.86	65
																	D	"	66/P	"	90.5	42	43	1.66	70
11	"	"	"	60	100	"	475	35	70.2	5/277	.026	41.9	"	27.2	55	93.6	126A	"	100/P	"	91.5	45	37	1.54	75
																	B	"	0	"	91.1	0	0		
																	C	"	33/P	"	91.3	39	28	1.85	62
																	D	"	66/P	"	91.3	37	35	1.72	72
																	E	"	123/P	"	91.5	47	43	1.60	76
																	F	"	77/0	"	91.1	52	42	1.45	69

BB

DEVEL. PROD. R/O / LAKED PAINT

30 J TAE-3

TSD #	MT	MIN TINT	MAX TINT	NB #	6	12	30	60	F.C.	6	12	30	60	F.C.
1	L+12	96	104	96	1.18	1.17	1.14	1.08	1.00	0.83	0.85	0.87	0.83	0.83
2	L+12	96	104	148A	1.20	1.21	1.20	1.20	1.00	—	—	—	—	—
	L+12	115	115	B	2.40	2.32	2.11	1.97	1.56	—	—	—	—	—
3	L+12	106	106	148C	2.13	2.00	1.85	1.76	1.59	—	—	—	—	—
	L+6	125	110	D	3.00	2.79	2.52	2.30	2.02	—	—	—	—	—
4	L+12	96	105	148E	1.67	1.63	1.56	1.51	1.28	—	—	—	—	—
	L+3	115	115	—	—	—	—	—	—	—	—	—	—	—
6	L+14		110	108A	1.69	1.58	1.52	1.46	1.15	1.17	1.18	1.14	1.15	1.07
	Dk2		120	B	3.00	2.90	2.72	2.52	2.03	0.96	0.96	0.95	0.96	0.91
7	L+8		99	112A	1.90	1.78	1.73	1.57	1.40	1.30	1.29	1.29	1.25	1.10
	Dk12		106	B	3.49	3.25	3.00	2.63	2.07	1.05	1.04	1.03	1.03	0.92
8	Dk2		104	116A	2.29	2.19	2.06	1.90	1.52	1.45	1.46	1.42	1.40	1.16
	Dk14		110	B	3.37	3.13	2.82	2.44	1.95	1.05	1.04	1.03	1.03	0.95
9	L+2		106	120A	1.55	1.49	1.44	1.34	1.13	1.25	1.50	1.26	1.23	1.07
	Dk12		114	B	2.68	2.53	2.29	2.13	1.83	1.05	1.04	1.03	1.03	0.93
10	L+8		98	124A	2.33	1.55	1.57	1.49	1.22	1.13	1.18	1.14	1.13	0.92
	Dk4		115	B	4.25	2.82	2.75	2.57	2.44	0.92	1.09	0.95	0.98	0.82
	L+8		101	C	2.33	1.59	1.68	1.57	1.29	1.21	1.21	1.16	1.15	0.94
	L+8		100	D	2.33	1.55	1.57	1.51	1.29	1.21	1.21	1.16	1.11	0.96
11	E		99	128A	2.49	1.68	1.71	1.65	1.33	1.21	1.21	1.19	1.15	0.96
	Dk14		115	B	4.61	3.05	3.00	2.70	2.67	0.88	0.96	0.89	0.89	0.78
	E		105	C	3.97	2.59	2.50	2.38	2.11	1.13	1.18	1.14	1.15	0.96
	L+2		103	D	3.00	2.05	2.07	1.97	1.67	1.17	1.18	1.16	1.17	0.96
	L+10		103	E	2.67	2.00	1.91	1.82	1.50	1.46	1.37	1.39	1.32	1.12
	L+10		98	F	1.54	1.55	1.44	1.41	1.16	1.29	1.27	1.32	1.30	1.17

BB

12

			FIRST STAGE							INTER-STAGE		SECOND STAGE				DEVEL. PROD.								
D #	ACID LOT	%Cl	MIXER	ACID FLOW	DIL. FLOW	DIL. %HCl	PRESS.	TEMP. OUT	ACID CONC.	STAT. DIA.	TIME SEC.	VEL. FPS.	H_2O FLOW	ACID CONC.	TEMP. OUT	% DTC	NB #	% ARO.	SEP. QTY/TIME	TEMP. °F	% DTC	270 VP	16 VP	PHASE	SPEC. SUCT.
12	448-1	4.01	B II	59	100	0	530	78	69.7	50/.527	0.407	10.2	20	26.2	71	94.0	130A	5	0/—	80/1	91.0	0	0		54
																	B	"	100/P	"	91.8	47	48	1.49	74
																	C	"	200/P	"	91.7	53	49	1.60	76
																	D	"	100/0	"	92.3	60	51	1.39	77
13	"	"	B III	30	50	"	350	65	69.2	50/.527	0.814	5.1	10	28.2	78	94.1	134A	"	0/—	"	91.3	16	0	—	
																	B	"	100/P	"	91.8	44	35	1.60	
																	C	"	200/P	"	91.9	49	36	1.72	
																	D	"	100/0	"	92.2	48	37	1.48	
14	"	"	"	30	48	"	310	85	70.7	17/.527	0.287	5.1	10	29.4	72	94.1	138A	"	0/—	"	91.0	10	0	—	
																	B	"	100/P	"	91.8	33	24	1.83	
																	C	"	200/P	"	92.3	44	27	1.64	
																	D	"	100/0	"	92.6	45	21	1.63	86
15	"	"	"	30	50	"	280	80	70.0	6/.430	0.071	7.04	10	29.2	72	94.5	142A	"	0/—	"	90.9	0	0	—	
16	"	"	"	"	"	"	"	"	"	2 h	1428	in Stream					B	"	100/P	"	91.9	29	19	1.74	
																	C	"	200/P	"	92.5	43	19	1.74	
																	D	"	100/0	"	92.4	37	15	1.70	
17	"	"	B II	60	100	5% Acid	450/470	75	69.8	50/.527	0.407	10.2	20	26.5	75	91.6	150A	"	100/0	80/1	92.8	53	42	1.52	
																	B	"	100/0	80/4	93.4	58	47	1.46	
																	C	"	100/P	80/4	92.8	52	43	1.62	
																	D	"	50/0	80/4	92.9	51	43	1.54	
18	"	"	"	60	100	0	420/440	—	69.0	50/.527	0.407	10.2	20 (5%)	34.7	—		154A	< 5	<100/0	80/1	91.9	38	36	1.57	
																	B	< 5	<100/0	80/4	91.8	48	36	1.56	
19	450-1	3.43	"	60	100	0	430/450	60	67.1	50/.527	0.407	10.2	20	25.4	60	93.7	158A	5	0/—	80/1	91.9	10	21	—	
																	B	"	100/P	"	92.4	46	49	1.47	
																	C	"	200/P	"	92.3	60	51	1.37	
																	D	"	100/0	"	92.0	57	52	1.52	

BB

LAKED PAINT

DEV. PROD. R/O / 30J TAE-3

TSD #	MT	MIN TINT	MAX TINT		NB #	6	12	30	60	F.C.		6	12	30	60	F.C.
12	Dk12		115		132A	2.19	2.12	1.98	1.86	1.72		1.04	1.00	1.03	0.98	0.85
	Lt10		97		B	1.43	1.42	1.40	1.36	1.19		1.21	1.17	1.21	1.18	0.98
	Lt10		97		C	1.00	1.03	1.02	1.04	0.86		1.21	1.20	1.24	1.16	0.97
	Lt12		97		D	1.00	1.03	1.05	1.04	0.86		1.13	1.10	1.13	1.10	0.93
13	Lt4		115		136A	1.75	1.73	1.67	1.57	1.40		1.00	0.97	1.00	0.96	0.83
	Lt12		95		B	1.07	1.06	1.07	1.07	0.90		1.21	1.17	1.18	1.14	1.13
	Lt14		100		C	1.18	1.12	1.12	1.13	0.88		1.21	1.17	1.18	1.14	1.13
	Lt14		100		D	0.96	0.97	0.98	1.00	0.88		1.08	1.07	1.11	1.08	0.93
14	Dk12		125		140A	3.33	3.16	2.68	2.47	2.03		1.09	1.07	1.05	1.04	0.97
	Lt6		100		B	1.60	1.58	1.46	1.45	1.15		1.36	1.29	1.30	1.24	1.15
	Lt6		100		C	1.53	1.53	1.43	1.42	1.14		1.32	1.25	1.27	1.22	1.11
	Lt6		100		D	1.47	1.47	1.39	1.39	1.10		1.23	1.18	1.19	1.18	1.07
15	Dk14		115		144A	2.80	2.68	2.37	2.16	3.00		1.00	1.03	1.03	1.04	0.92
	Lt6		102		B	2.40	2.32	2.15	2.00	1.70		1.25	1.28	1.28	1.23	1.15
	Lt6		102		C	2.33	2.16	2.00	1.89	1.56		1.25	1.21	1.23	1.19	1.03
	Lt12		106		D	2.20	2.16	2.00	1.89	1.65		1.13	1.17	1.18	1.15	1.03
17	Lt14		105		172A	1.85	1.61	1.50	1.44	1.15		—	—	—	—	—
	Lt14		103		B	1.69	1.50	1.42	1.39	1.08		—	—	—	—	—
	Lt10		104		C	1.85	1.67	1.58	1.50	1.20		—	—	—	—	—
	Lt14		105		D	1.69	1.56	1.46	1.39	1.15		—	—	—	—	—
18	Lt8		100		174A	2.31	2.11	1.96	1.81	1.48		—	—	—	—	—
	Lt10		101		B	2.31	2.11	2.00	1.89	1.54		—	—	—	—	—
19	Dk2		108									—	—	—	—	—
	Lt10		100									—	—	—	—	—
	Lt10		100									—	—	—	—	—
	Lt12		99									—	—	—	—	—

BB

	FIRST STAGE									INTER-STAGE		SECOND STAGE				DEVEL. PROD.								
TSD #	ACID LOT	% ACE	NOZ.	ACID FLOW	OIL FLOW	OIL % ACE	PRESS. lbs/in²	TEMP. OUT	ACID CONC.	LGTH/ ASV.	TIME SEC.	VEL. FPS	H_2O FLOW	ACID CONC.	TEMP OUT	% CRC	NOZ #	% ACID	SPRAY QTY.	TEMP. °F	% CRC	27° VP	16° VP	Phase	Spec. Surf.
20	450-1	3.43	BII*	31	100	35.2	50/70	52	68.8	50/.527	0.59	7.06	14.5	25.6	53	94.5	160A	4.2	70/0	80/1	92.9	49	36		86
																	160B	4.2	85/0	80/1	92.9	53	40		87
21	450-1	"	BII*	31	100	34.6	40/60	—	67.6	50/.527	0.59	7.06	14.5	25.3	70		164D	4.2	85/0	80/1	93.1	45	36	(to Storage)	
	blue R																								
25	450-1	"	BII*	56	100	35.5	60/90	63	74.8	50/1.05	2.67	1.78	14.5	31.8	65	93.9	180A	5.0	50/0	80/1	92.6	51	45		
																	B	"	100/0	"	93.6	55	47		80
																	C	"	150/0	"	91.9	58	48		85
26	450-1	"	BII*	40	100	35	60/90	—	70.6	50/.527	0.52	8.01	14.5	29.3	55	95.1	184A	5.0	50/0	80/1	92.4	46	40		
																	B	"	100/0	"	93.2	53	40		78
																	C	"	150/0	"	92.6	58	43		
27	476-1	"	BII*	31	100	35	40/70	70	67.7	480/1.0	26		14.5	21.4	42	94.3	188A	7.0	70/0	80/1	89.7	58	51		
																	B	"	140/0	"	89.3	55	50		
																	C	"	209/0	"	89.7	57	47		
= BLUE R — 26 thru 31																									
32	476-1	"	BII*	56	100	35.3	60/80	87	73.4	50/1.05	2.67	1.75	14.5	31.5	66	95.0	2A	5.0	100/0	80/1	91.1	54	44		
33	"	"	"	"	"	36.2	60/85	86	73.1	"	"	"	"	31.9	64	95.1									
34	476-1	"	BII*	"	"	35.3	60/90	83	72.1	"	"	"	"	30.2	64		6A	Start 5.0	100/0	80/1	92.0	55	43		
																	B	Working 2.0	"	"	91.0	57	46		
																	C	Finish 5.0	"	"	91.7	57	44		
35	476-1	"	BII*	56	100	35.0	60/90	85	73.4	"	"	"	"	32.2	67		10A	5.0	100/0	80/1	92.0	56	50		
																	B	2.0	"	"	95.2	56	44		
																	C	0.0	"	"	95.5	55	45		
																	D	0.6 Start 7.4 End	"	"	94.9	54	44		

* ACID NOZZLE CLEARANCE INCREASED TO 35 MILS.

BB

DEV. PROD. R/O

LAKED PAINT

TSD #	MT	MIN TINT	MAX TINT		N/B #	30J 6	12	30	60	F.C.	Hrs	TAE-3 6	12	30	60	F.C.	Hrs	Lake R,O MT	MIN TINT	MAX TINT
					1576															
20 ✓	DK10		99		162A	1.95	1.95	1.87	1.70	1.42	48	1.14	1.03	1.08	1.06	1.06	72	DK 99		100 R D
	E		100		B	1.55	1.54	1.50	1.43	1.15	"	1.09	1.00	1.03	1.02	0.93	"	DK 29		100 R D
21																				
25 ✓	Lt 8		100		182A	1.57	1.56	1.54	1.52	1.13		1.00	0.96	0.97	0.98	0.89	72	DK 15		96
	Lt 10		100		B	1.43	1.33	1.38	1.33	1.05		0.91	0.93	0.95	0.96	0.88	"	DK 5	90	96
	Lt 14		100		C	1.36	1.33	1.33	1.27	1.03		0.86	0.86	0.89	0.90	0.82	"	DK 5		96
26	Lt 6		106		186A	3.09	2.93	2.74	2.75	2.06	72	1.04	1.03	1.05	1.08	0.90	72			
	Lt 10		103		B	1.64	1.64	1.58	1.67	1.22	"	0.96	0.97	1.00	1.02	0.88	"			
	Lt 14		100		C	1.55	1.50	1.48	1.54	1.12	"	0.92	0.90	0.95	0.96	0.88	"			
27	Lt 16				190A															
( )	Lt 16				B															
	Lt 16				C															
					1960															
32	42		96	Small Thirsty Oasis	4A															
33					B															
				125P 115P	C															
					D															
				Thirsty Oasis LSP HSP	E															
					F															
					G															
34	Lt 5		100		5A							9 / 11	135/135	15/175	23/22.5	51/95				
	Lt 5		99		B							11	135	175	22.5	79				
	Lt 5		100		C							11.5	14	15.5	23.5	52				
35	Lt 8 Lt 9		104 100		187	11/8	15/10	20/14	26/15.5	57/29		17 / 11	135/135	15/175	23/22.5	50/95		DK 3		99
	Lt 10 Lt 5		102 105		B	9.5 -	12 -	16.5 -	22 -	53 -		25	15	195	25	55		DK 12		106
	DK 99 DK 99		150 -		C	7 "	9 "	11.5 -	17 "	46 "		11	14	17	23	55		DK 99		150
	DK 99 2X 99		130 -		D	8 -	10.5 -	14 -	19 -	46 -		9	12	16	21	50		—		

BB

First Stage / Interstage / Second Stage

TSD #	[illegible]	2.Cl	Mix	[illegible]	Def [illegible]	Def [illegible]	[illegible]	Temp [illegible]	Acid Conc.	[illegible]	Time [illegible]	Vel FPS	H_2O Flow	Acid Conc.	Temp	% [illegible]	NB #	% Acid	[illegible]	Temp [illegible]	[illegible]	27°	15°		[illegible]
																	1860	Acid							
36	0047%	343	BIII*	56	100	33.9	50/90	84	71.6	57/1.05	2.67	1.78	19.5	31.7	63	—	12	5.0	100/0	80/1	92.2	53	44		
37	•	"	"	31	"	"	20/50	90	67.7	50/.527	0.590	7.06	"	23.4	50	—	14A	4.2	85/0	80/1	92.4	50	39		
38		"	"	31	"	"	"	84	68.0	"	"	"	"	24.6	50	—	16A	4.2	25/0	80/1	92.7	30	30		
39	0049% 1+2	"	"	"	"	"	30/60	85	69.1	"	"	"	"	26.2	50	—	20			"		43	36		
40	"	"	"	"	"	"	30/60	85	65.9	"	"	"	"	26.1	50	—	22			"		45	44		
41	00457	"	"	"	"	34.9	50/90	75	67.5	"	"	"	12.8	25.5	46	—	24A	4.7	100/0	"	92.2	45	34		
42	"	"	"	"	"	"	57/70	80	69.1	"	"	"	"	25.7	47	—	26A 26B	5.9 5.0	115/0 100/0	" "	90.4 91.9	45 46	35 36		?
43	"	"	BII 70 ml	60	100	[illegible]	400/420	107	65.5	57/1.05			"	25.8	65	—	25A B	5.0 "	100/P 200/P	50/2 "		55 55	48 50		68 75
44	"	"	"	60	67	"	350/395	110	73.6	"			"	29.9	69	—	30A B	" "	150/P 200/P	" "		52 57	49 49		75 77
45	"	"	BIII	30	50	"	200/220	112	69.1	50/.527	0.514	5.1	"	21.3	50	to 11.	40A	"	200/P	80/1	91.8	52	51		77
—	46	47 + 48 — Blue R —																							
49	00457	3.43	BII 15 ml	62	24	H_2O	375/350	82	78.5 (green?)	57/1.05			12.7	30.8	65	—	34A B	" "	100/P 200/P	50/2 "	90.6 90.9	26 27	37 37		60 59
50	"	"	"	60	48-45	"	340/370	95	76.0 (al green)	"			"	31.3	75	—	36A B	" "	150/P 200/P	" "	91.3 92.1	54 55	45 50		73 76
51	00457 30456	"	BII 35 ml	60	66	"	30/70	101	74.1	"				29.8	64	.	38A B	" "	100/P 200/P	" "	91.5 91.5	56 56	55 59		71 72

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DUP050082161

BB

Leaked in Paint

VSD#	MT	MIN Temp	MAX Temp		KB	6	12	30	60	F.C.		6	12	30	60	FC	MT	Max Temp	Min	%CPC
	Devel Rigid RO (M623 73451)				30J							TAE-3					Lake RO.			
					1860															
36	Lt14	—	102																	
37	DK2	96 RD7	100 RD5																	
38	DK3	—	100 RD																	
39	DK3	—	105																	
40	DK3	—	105																	
41	DK7	—	98 RD20																	
42	DK2	—	96 RD20																	
43	Fg Lt3		97RD 95RD		32A 32B	15/5 15.5 "	21/10.5 22 "	25/14 25.5 "	36/15 36.5 "	94/57 98 "							DK20 DK20	112 RD 112 RD		86.2 87.7
44	DK4 DK5		94RD 92RD		32C 32D	19 " 18 "	23 " 22 "	29 " 29 "	37 " 37 "	132 " 100 "							DK29 DK29	114 [illegible] 114 RD		88.8 85.4
45	Lt12		107RD		42C	14 "	17.5 "	24 "	31 "	67/52							Lt10	110 RD		
49	Lt99 Lt99		130 — 130 —		— —															
50	DK4 DK2		95RD 94 " "		42A 42B	16/8 15.5 "	14.5/10 12.5 "	26/8 29 "	34/15 37 "	25/52 53 "							DK25 "	111 RD 112 " "		
51	[illegible]		106RD " " "		46A 46B															

DUP050082162

BB

2

			First Stage							Interstage			Second Stage			Development									
TSD II	Acid Lot	% Cl	Mixer	Acid Flow	Dil Flow	Dil ?	Press	Temp out	Acid Conc	Lgth/Dia	Time sec	Vel	H_2O Flow	Temp out	Conc	NB #	% Agent	Sol'n qty/type	Temp/Time	% CPC	27° VP	15° VP		SP cont	
52	00486-1 9/1	3.43	BII 15 mil [illegible]	60	66	H_2O	150/200	96	74.4	57/1.05			12.5	65	31.7	1860 44A 44B	Argard 5 5	200/P 200/P	83/2h 83/2h	91.4 91.6	57 55	49 47		77 76	
53	"	"	" 15 mil	40	42	"	70/135	103	73.0	57/1.05			"	56	24.8	48A 48B	7.3 5	270/P 270/P	83/2h -	89.4 91.5	62 59	50 53		70 68	
54	"	"	13 mil	40 Blowcase	46 650 psi	"	80/110	109	72.5	57/1.05			8.5	80	33.3	52A 52B 52C	4.6 5 "	185/P 180/P 200/P	83/2h " "	91.7 92.1 92.1	55 51 51	53 53 54		72 70 73	
55	"	"	"	34 Blowcase	30 400 psi	"	105/150	100	74.5	57/1.05			8.5	74	35.5	TSJ.J.		—	—	—	—	—			
56	"	"	" 12 mil	40 Non control	44 valves	"	120/150	92	73.5	144/1			"	65	33.4	60A	5	200/P	80/2h	91.5	59	52			
57	[illegible] Pat 10/1	2.6	BII/12	32/20	35/7	"	50/75	111	72.1	57/1.05			[illegible]	50	26.6	64A 64B 64C 64D	6 " " 5	200 " " 200	" " " "	88.5 89.4 90.1 91.5	63 65 65 65	60 69/23 63/6 60	[illegible]	[illegible]	
55	"	2.6	" "	32/18	35/18	"	50/75	111	73.1	57/1.05			6.5	74	35.9	66A 66B 66C 66D 66E	5 " " " "	200 " " " 180	80/2 " " " "	91.9 91.3 91.8 92.3 91.5	60 65 62 61 61	55/0 63/17 63/21 55/14 51/0	+17, [illegible] +37, [illegible] +13% N [illegible]	[illegible]	
																66F 66G	" "	" "	" "	91.7 92.0	58 63	62/14 62/17	+17% [illegible] +37% N [illegible]	[illegible]	
59	"	2.6	plugged " /10	32/23	35/20	"	80/110	109	72.3	57/1.05			6.8	75	35.0	68A	5	200	80/2	91.7	68	66/0			
60	"	2.6	BII/10 cleaned	32/23	35/20	"	52/85	108	72.7	57/1.05			6.8	79	35.0	70A 70B 70C 70D	5 " " "	100 " 200 "	80/2 " " "	90.5 90.5 90.5 91.6	55 57 64 65	54/0 55/17 62/0 66/19	+27% N [illegible] +27% N [illegible]		

BB

						30J						TAE3					Lake Ro. nBr-254-D95090						
TSD #	MT	Min Tint	Max Tint		NB #	Grn	12	30	60	FadC		Grn	12	30	60	FadC	MT	Tint Min	Tint Max	%CPC	BT NB		
( ) 52	Lt20		100 R	7.5	1860																		
	"		" "	0 =	50A	9.5/5.5	11/6.5	15/9.5	20/11.5	35/32		11.5/11.5	12.5/14	15/15	21.5/23	46/53	Lt10		94 R5D				
				5 =	50B	9.5	11.5	15.5	20	"		11	12	12	21	45	Lt10		94 R10				
				10 =	50C	9	10.5	14	15	"		5.5	10.5	14	15	41	Lt10		94 R5				
53			102 R														—		—				
	Lt12		104 RD		56A	22/?	25/25	41/32	56/51	39/39		9.5/10.5	11.5/11.5	15.5/16.5	11.5/22	42/50	Lt35		98 RD				
54	Lt10		102 RD		54A	8.5/7.5	10.5/9.5	15.1/11.5	21/18.5	56/55		12.0/10.5	12.5/13	17/17.5	23/23	45/51	Lt39		95 R5D10	87.4			
					54B	" "	11 "	15.5 "	" "	57 "		9.5 "	12 "	11.5 "	" "	46 "	Lt29		95 " "	88.4	58B	Lt29 Sk	R29 D29
					54C	" "	11 "	" "	" "	55 "		9.5 "	12 "	17.5 "	" "	46 "	Lt29		95 " "	55.6	58C	"	" "
56	Lt20		106 RD		62A	24/?	32/25	45/26	85/51	43/39		9.5/10.5	12/11.5	16/16.5	21.5/22	45/50	Lt29		96 RD				
( ) 57	Lt29,97		RD		—																		
	"		WR+GI		—																		
	"		RD		—																		
	"		RD		—																		
58	Lt29		110 RD		75A	7/5.5	10/7.5	13.5/10	18/14	35/36		7.5/10	12/12	14/16	19/21.5	37/44							
	Lt30		106 RD		75B	6 "	8 "	10 "	14 "	36 "		6 "	8 "	11.5 "	16 "	35 "							
	Lt29		" GI		75C	5 "	7 "	10 "	13 "	35 "		6 "	8 "	11.5 "	16 "	34 "							
	Lt23		104 RD		75D	— "	— "	— "	— "	broke		—	—	—	—	— "							
	Lt29		150 RD		75E	6.5 "	9 "	12.5 "	17 "	39 "		7 "	9.5 "	13 "	12.5 "	37 "							
	Lt29		124 RD		75F	6 "	7.5 "	10.5 "	19.5 "	36 "		5.5 "	5.5 "	12 "	16.5 "	35 "							
	Lt31		106 E		75G	5 "	6.5 "	9 "	13 "	34 "		5.5 "	7.5 "	11 "	15 "	35 "							
59	Lt29		100 RD		—																		
( ) 60	Lt35		110 RD		80A	7 "	9.5 "	13.5 "	17.5 "	35 "		7 "	9 "	12.5 "	17.5 "	37 "							
	"		106 GD		80B	5 "	5.5 "	9 "	13 "	34 "		6.5 "	8.5 "	11.5 "	16 "	34 "	Lt35		92 GI				
	"		100 RD		80C	7 "	5.5 "	12 "	16 "	37 "		7 "	9 "	13.5 "	15.5 "	37 "							
	"		106 GD		80D	5 "	6 "	9 "	11.5 "	35 "		6 "	8.5 "	11 "	15.5 "	35 "	Lt35		92 GI				

DUP050082164

3B

TSD #	Acid Lot	%?	Mixer	Acid Flow/Rec	H2O Flow/Temp	Press	Temp out	Acid conc	Lgth/Dia	Time sec	Vel	H2O Flow/Temp	Temp out	Conc out	NB #	% Agent	Solv Ov/Type	Temp Time	% C/C	V.C. 27°15'	%B	Remarks		Sp tarf.
			First Stage						Interstage			Second Stage			Development									
															1860	Argued								
61	00001-1	2.6	BII/Small	32/23	35/18	70/100	109	71.5	57/1.05			6.5/7	70	34.4	72 A	5	100/P	80/2hr	90.9	60/54	0			
															72 B	"	"/"	" "	91.4	62/58	19	+2% N797		
															72 C	"	200/"	" "	91.2	62/59	0			
															72 D	"	"/"	" "	92.1	65/63	19	+2% N797		
62	"	"	"/"	40/23	44/21	110/140	108	73.3	"/"			9.5/9	68	33.2	74 A	5	50/P	80/2	91.1	60/59	0			
															74 B	"	100/P	" "	90.5	58/57	0			
															74 C	"	200/P	" "	90.8	62/56	0			
															74 D	"	100/P	" "	92.0	60/58	17	85 BB / 15 BGS		
															74 E	"	100/P	" "	90.5	64/65	18	2% N797		
															74 F	"	100/P	45 "	90.3	62/62	18	" "		
63	"	"	"/"	50/26	55/19	175/195	110	73.8	"/"			10.6/5	67	32.5	76 A	5	50/P	80/2	90.5	61/59	0			
															76 B	"	100/P	" "	91.1	58/53	0			
															76 C	"	200/P	" "	90.6	64/57	0			
															76 D	"	100/P	" "	92.0	60/53	16	85 BB / 15 BGS		
															76 E	"	100/P	" "	90.6	64/60	15	2% N797		
															76 F	"	100/P	45 "	90.4	64/60	18	" "		
64	00031-1 / 00031-2 / 00032-1	"	"/"	50/24	55/21	190/200	110	74.5	144/"			10.6/5	70	33.7	88 A	"	100/P	80/2	90.4	64/55	0			
															88 B	"	200/P	" "	90.4	61/55	0			
															88 C	"	100/P	" "	91.8	60/57	17	85 BB / 15 BGS		
															88 D	"	100/P	" "	91.0	61/63	15	2% N797		
															88 E	"	100/P	45/2	90.1	62/60	16	2% N797		
															88 F	"	150/P	70/2	90.1	63/61	14	1.5% N797		
															88 G	"	150/P	50/2	91.2	65/66	16	2% N797	Lux (?)	
65	00002-1	"	"/"	50/23	55/15	170/190	105	73.6	144/"			10.6/4	67	33.9	92 A	"	100/P	80/2	89.7	62/56	0			
															92 B	"	100/P	" "	90.3	61/61	15	1.5% N797		
															94 A	"	100/P	80/2	89.9	60/61	18	2% N797		
															94 B	"	100/P	80/1	89.4	62/62	16	2% "		
															94 C	"	100/P	80/4	89.8	64/65	18	2% "		
															94 D	"	100/P	80/7	90.4	63/63	21	2% "		
				66	Blue R																			

DUP050082165

BB

					30J					TAE3					Lake Ro. nBF-254-D95090		
TSD #	MT	Min Tint	Max Tint	NB #	GRPM	12	30	60	Fnd C.	GRPM	12	30	60	Fnd C.	MT	Time Min	Time Max
				1760													
61	Lt25	110 RD		82 A	8.5/8.5	10.5/7.5	14/10	19/14	41/36	7.5/10	10/12	14.5/16	19.5/21.5	39/44			
	Lt25	135 GD		82 B	5 "	7 "	10 "	13.5 "	35 "	6 "	8.5 "	12 "	16.5 "	35 "	Lt15		92 GI
	Lt25	100 RD		82 C	—	—	—	—	broke	—	—	—	—	—			
	Lt[illegible]	105 GD		82 D	5 "	6.5 "	9.5 "	13.5 "	35 "	6 "	8.5 "	12 "	16.5 "	36 "	Lt15		92 GI
62	Lt12	100 RD		84 A	9/5	12/7	17/10.5	22/14	49/35	10.5/10	13/12.5	15/17.5	25/23.5	59/56			
	Lt12	100 RD		84 B	7	10	15	19	44	9.5	12.5	15	25	59			
	Lt12	100 RD		84 C	9	12	16.5	22	47	10	13	15.5	25	60	Lt9		91 GI
	Lt15	100		84 D	6	9.5	12.5	15	41	8.5	[illegible]	15	23.5	55	Lt9		92 GI
	Lt20	106 GD		84 E	5	8.5	7.5	16	42	8	10.5	13	23.5	56	Lt2		92 GI
	Lt[illegible]	104 G		84 F	6.5	10	10.5	15.5	44	9	11.5	16.1	22	55			
63	F[illegible]	97 R[illegible]		86 A	10	13	17.5	23	57	9.5	13	15	25	63			
	F[illegible]	97 R[illegible]		86 B	10	13.5	15.5	24	52	9	12.5	15	25	59			
	F9	[illegible] R[illegible]		86 C	5.5	12	16.5	22	49	9.5	12.5	17.5	21.5	53			
	Lt8	101 GT		86 D	6	10	13	15	42	8	11	15.5	22	54	DK6		94 GI
	Lt12	105 [illegible]		86 E	7	10.5	14	19	46	8.5	11.5	12.5	22.5	55	DK10		94 GI
	Lt10	103 GI		86 F	6.5	10	11.5	15	45	5.5	11.5	12.5	22.5	52	DK6		94 GI
64	Lt8	100 RD		90 A	7.5	12	16	21	47	5.5	11.5	16	21.5	52			
	Lt8	[illegible] RD		90 B	8	11.5	16	21	47	6.5	12	17	23	55			
	Lt13	101 ED		90 C	6	10	13	15	42	7	9	13.5	15	46	DK2		94 GI
	Lt10	102 [illegible]		90 D	5	[illegible]	13	17	42	7	10	14	20	49	DK2		96 GI
	Lt10	103 [illegible]		90 E	7	10.5	[illegible]	19.5	45	8	11	15.5	21.5	[illegible]	DK6		96 GI
	Lt12	104 E[illegible]		90 F	7	[illegible]	13.5	17	44	7.5	10	14.5	19.5	48	DK1		96 GI
	Lt15	102 ED															
65	DK2	100 RD		100 A													
	Lt10	104 FE		100 B													
	Lt10	104 G		100 C													
	Lt9	103 G		100 D													
	[illegible]10	107 GI		100 E													
	[illegible]12	107 GD		100 F													

DUP050082166

BB

TSD #	Acid Lot	%Cl	Mixer Cl	Acid Flow/Temp	H2O Flow/Temp	Press Hold/Acid	Temp out	Acid conc	Lgth/Dia	Time sec	Vel	H2O Flow/Temp	Temp out	Conc out	NB #	% Agent Amount	Soly Ctl/Type	Temp Time	% PC	VP 27°/75°	% B	Remarks		Sp sort
67	00012-1	2.6	BII/Fmi	50/22	55/50	170/200	122	72.9	144/1.05			10.6	70	33.1	96A	5	100/P	50/2	89.0	64/64	0			
															96B	5	100/P	50/2	89.7	63/64	14	2% N[illegible]		
															96C	5	100/P	53/4	90.2	66/65	18	2% N[illegible]		
															96D	5	100/P	50/2	90.6	65/62	17	[illegible]		
65	00012-1	2.6	BII/Fmi	50/20	55/95	210/230	134	72.4	144/1.05			10.6	85	33.1	95A	5	100/P	50/-	88.5	61/59	0			
															95B	5	100/P	50/2	89.5	64/64	17	2% N[illegible]		
															95C	5	100/P	50/4	92.7	66/66	17	2% N[illegible]		
															95D	5	100/P	50/-	90.3	62/63	16	[illegible]		
69	— BLUE R —																							
2/4 70	00012-1	4.0	BII/Fmi	50/23	57/54	200/210	118	72.3	144/1.05			10.6	75	33.0	110 A	5	100/P	50/2	91.2	51/50	0		(3,957.0)	75
															110 B	5	"	"	91.6	53/53	11	12 BGS	11,83	77
															110 C	5	"	"	91.9	49/51	16	12 "	85 "	77
															110 D	5	"	"	92.1	53/47	17	15 "	85 "	80
															110 E	5	"	"	90.1	56/55	13	19% N[illegible]		76
															110 F	5	"	"	91.0	54/55	15	29% N[illegible]		73
2/9 71	00012-1	4.0	BII/Fmi	50/23	55/12	170/190	102	73.0	144/1.05			10.6/70	70	33.5	114A	5	100/P	50/2	90.7	53/47	0		(4,032.0)	76
															B	5	100/P	50 "	91.2	54/48	6	5% BGS		73
															C	5	100/P	50 "	90.5	54/50	12	7% "		73
															D	5	200/P	50 "	91.5	57/56	11	7% "		77
															E	5	150/P	50 "	90.5	52/49	9	4.2 N[illegible]		—
															F	5	100/P	50 "	90.6	54/51	15	1% "		73
2/10 72	— BLUE R —																							
2/11 73	00012-1	4.0	BII/SJ	50/23	55/12	390/390	104	73.3	144/1			10.6/7	70	33.7	116 A / B	5	100/P	50/2	91.5	51/45, 46/37, 44/35	10, 8, 5	4.7 N[illegible]		
2/12 74	00012-1	4.0	BII/SJ	57/23	56/11	230/245	108	72.9	144/1			10.6/7	70	33.7	118A	5	100/P	50/2	91.0	51/45	0	4.7 N[illegible]		80
2/13 75A	00012-1	4.0	BII/SJ	50/22	55/12	450/400	108	72.1	144/1			10.6/7	69	—	To J.J.					45/44	9			
" 75B	"	"	"	"	"	420/420			144/1											50/41	0			
2/17 76	——		Blue R		To	GG																		
2/17 77	——		Blue R		To	J.J																		

67

DUP050082167

BB

TSD #	MT	Min Tint	Max Tint		NB #	GRM (30J)	12 (30J)	30 (30J)	60 (30J)	Fadc (30J)		GRM (TAE3)	12 (TAE3)	30 (TAE3)	60 (TAE3)	Fadc (TAE3)	MT (Lake Ro.)	Min Tint (Lake Ro.)	Max (Lake Ro.)
		~ N523				30J						TAE3					Lake Ro. nBF-254-D95090		
67	Lt^{6}		95 RD		102A	Samples got mislabeled + confused so discarded all.													
	Lt^{12}		95 G D		102B														
	Lt^{4}		101 G D		102C														
	Lt^{16}		95 G D		102D														
68	Lt^{9}		102 RD		104A														
	Lt^{29}		105 G D		104 B														
	Lt^{19}		106 G D		104 C														
	Lt^{17}		105 G D		104D														
70	Lt^{13}		104 RD		112A	7.5/7.5	10.5/10	15.5/12.5	21.5/19	51/51		10.5/10	13/12.5	15/12.5	23.5/21.5	44/43	Lt^{6}	—	94 RD
	Lt^{13}		104 G		112B	7	17	14	19.5	50		7.5	10.5	14.5	19	39	Lt^{13}	—	95 G
	Lt^{19}		104 G		112C	6	9	13	18	43		7.5	10	14	15.5	38	Lt^{14}	—	96 G
	Lt^{27}		109 G		112D	6	9	13.5	15.5	45		7.5	10	10.5	15	35	Lt^{15}		95 G
	Lt^{13}		106 G		112E	7.5	13	14.5	20	51		8	10.5	14	15.5	45	Lt^{6}		98 GE
	Lt^{20}		106 G		112F	6.5	9	13	15.5	48		7.5	13	13.5	15	39	Lt^{4}		97 G
71	Lt^{16}		106 RD		126A	10/6.5	13/8	17.5/11.5	23.5/16	55/41		7.5/6	10.5/8	13/10	17/13	26/24	Lt^{3}	—	~94 RD
	Lt^{15}		106 G D		126B	9	12	16	22	52		7	9	12	15	25	Lt^{7}	—	~94 RD
	Lt^{25}		106 G D		126C	8	11	15	21	49		6.5	8.5	11	14	24	Lt^{5}	—	~94 RD
	Lt^{15}		106 G D		126D	8.5	11.5	15.5	21.5	50		6.5	5.5	10.5	14.5	24	Lt^{5}	—	93
	Lt^{15}		106 G D		126E	7.5	11	15	22.5	49		6.5	5.5	11	14.5	24	Lt^{5}	—	95 E E
	Lt^{15}		107 G D		126F	7.5	10	13.5	15.5	45		5.0	7	9	11.5	21	Lt^{4}	—	96 G D
72																			
73	Lt^{4}		103 G D																
74	Lt^{6}		104 G D		120												DK^{5}		100 E E
75 1/2																	—		
76																			
77																			

DUP050082168

VIII. APPENDIX

cc: M.Hunt/E. Gonick - Wilmington
F. R. Ortolani - "
W. Struve - Newark, N.J.
J. W. Minnich - Newport
J. F. Maurer - "
W. A. West - "
P. H. Griswold - "
W. L. Monson - "
J. E. Macrum - Newport

Newport, Delaware
August 22, 1969

FOR DU PONT USE ONLY

Dr. R. H. Wetzel
Pigments Dept.
Newport

BULLET MIXER - PATENT STATUS

At the Newport Colors Steering Meeting on 8/22/69 in discussion of two stage drowning of CPC (Case No. CP-106), the question of patent status of the Bullet Mixer was raised.

I asked Engineering Department what they had done and was advised by Rollin D. Morse, of Engineering, that their patent attorney, H J. McCauley, had determined that prior art would prevent them from obtaining a patent on the mixer, when this was considered in 1958 and 1961.

We might wish to consider process type claims incorporating the Bullet Mixer, with very specific limitations as to rates of flow, pressures, viscosities, concentrations, etc. However, we might be disclosing more than we would protect, and no disclosure of the Bullet Mixer, per se, would be preferable.

R. D. Nutting
Patent Manager

/aj

Extra

E. I. DU PONT DE NEMOURS & COMPANY

PIGMENTS DEPARTMENT

cc: R. H. Wetzel
J. F. Maurer
J. W. Minnich
Research File

Newport, Delaware
July 18, 1969

MESSRS: W. A. WEST
D. F. REDDISH
P. H. GRISWOLD.
P. J. ROACH
F. L. REIG
B. D. CRAIG
W. T. MC CRACKEN
C. STIGLIANO

RESEARCH - COLORS - NEWPORT

PRE-STARTUP SURVEY

SEMI-WORKS TWO-STAGE DROWNING UNIT

You are requested to attend a Pre-Startup inspection today at 1:00 P.M. in Lab 307, A-21 Bldg. The unit to be inspected is described in the attached write-up.

W. L. Monson

W. L. MONSON
RESEARCH DIVISION

WLM/mc

Newport, Delaware
July 18, 1969

PRE-STARTUP SURVEY

SEMI-WORKS TWO-STAGE DROWNING UNIT

LOCATION: Bldg. A-21, Lab 307

PERSONNEL RESPONSIBLE: W. L. Monson, B. D. Craig

I. OPERATION TO BE PERFORMED

Continuous two-stage drowning of CPC/H_2SO_4 solution.*

*First-stage water and acid are pressurized to 600 psi in blowcases and throttled to the first stage of the mixer. The first-stage product flows to the second stage where it mixes with a stream of water from the pump. The mixtures flow into a collecting drum under the mixer.

II. EQUIPMENT (See Sketch)

1. Two 5-gallon, 316 S/S blowcases, of 8" Sched. 80 pipe.
2. Two F&P S/S magnetic flowmeters, 1500 psi rating, for compressed N_2 to blowcases.
3. Nitrogen cylinder station. Pressure regulator system to provide 50 SCFM N_2 at 600 psi.
4. Two-stage mixer block.
5. Second stage water pump, (1/2 HP, 110 V Jabsco) and 10-gallon supply tank.
6. Control valves. Check valves, Vent and relief valves.

III. SERVICE FACILITIES

Uses 110 V electricity for second-stage water pump.

IV. HAZARDS

1. High pressure.
2. Concentrated sulfuric acid.
   a. Splashing and squirting.
   b. Mixing with water in wrong place.

V. SAFEGUARDS

Hydrostatic test.

Overpressure relief valve.

Check valves.

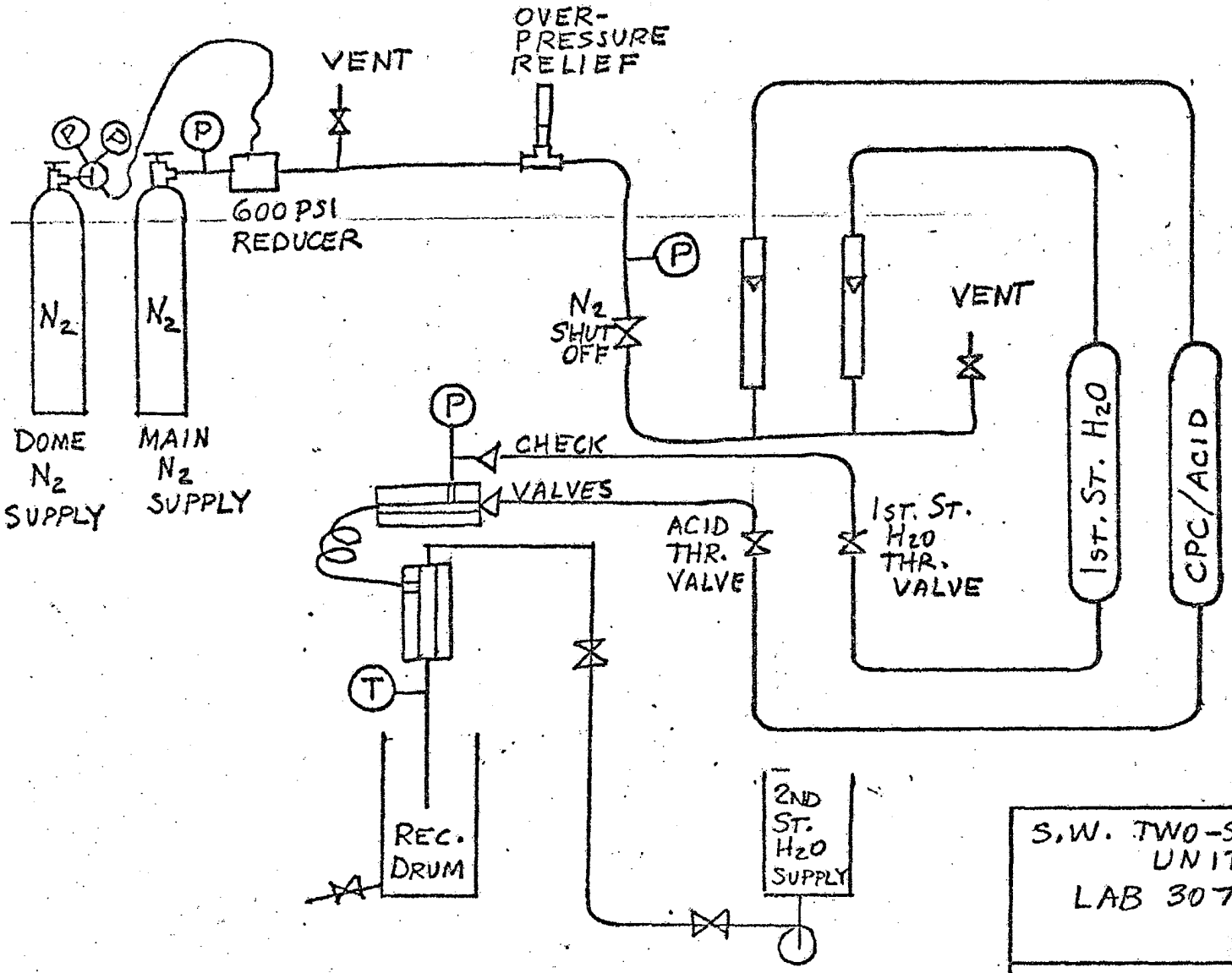
Splash shield.

VI. PROTECTIVE EQUIPMENT

Safety Shower
Safety Goggles
Safety Shoes
Safety Gloves
Face Shield

/mc

HYDROSTATIC TEST PRESS.	1000 PSI
OVERPRESSURE RELIEF SET	750 PSI
OPERATING PRESSURE	600 PSI



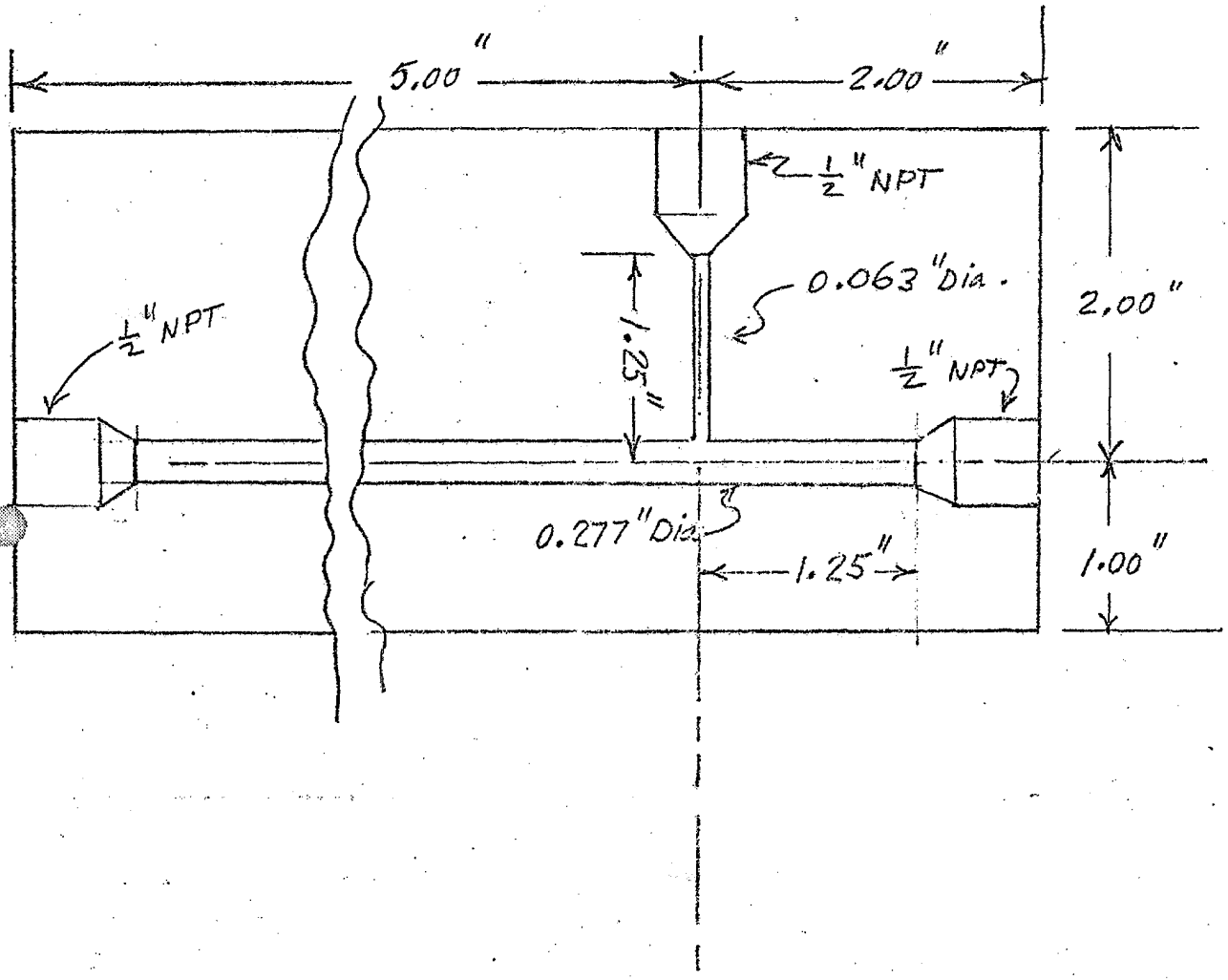
S.W. TWO-STAGE DROWNING UNIT
LAB 307, A-21

WLM
7-18-69

DUP050082174

1ST STAGE MIXING BLOCK

3" x 7" x 1½" S/S

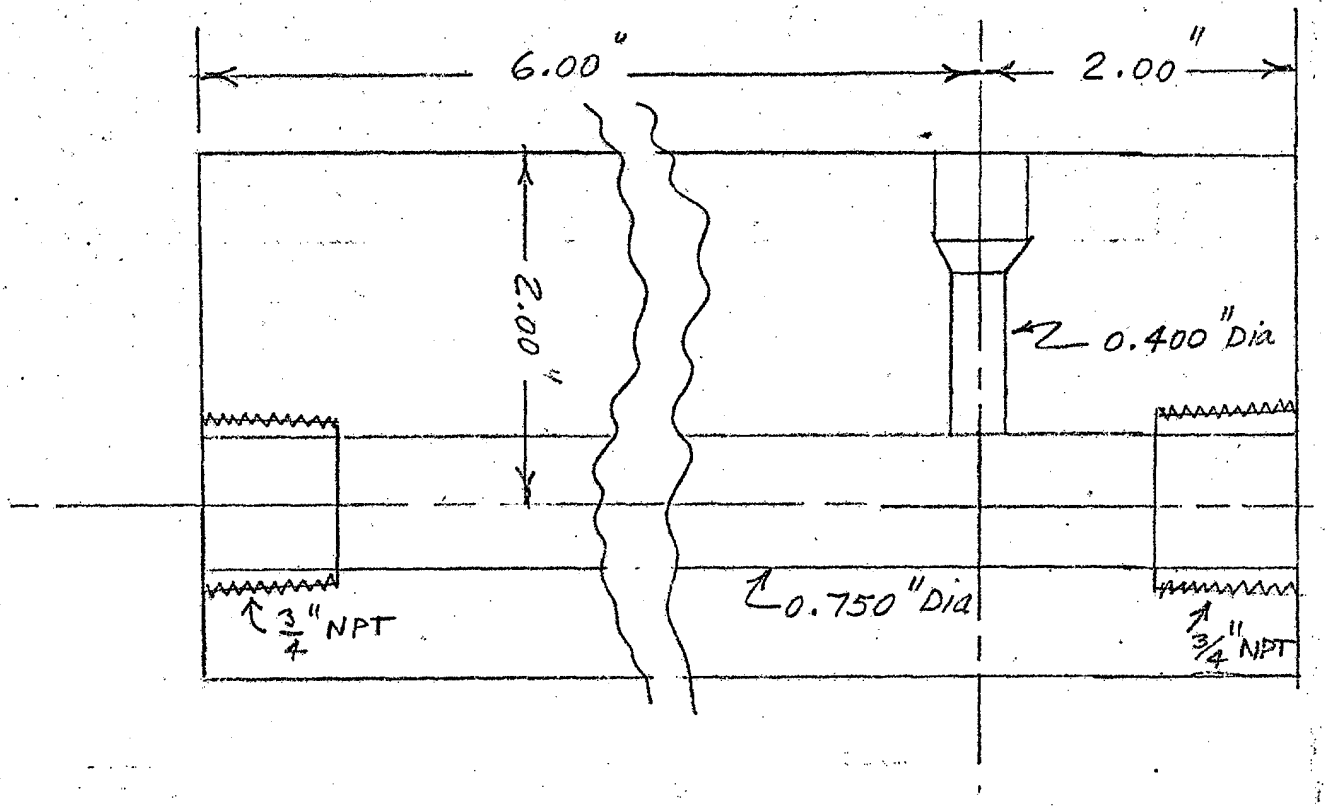


WLM
7-1-69
REVISED

DUP050082175

2ND STAGE MIXING BLOCK

2" X 3" X 8" 5/5



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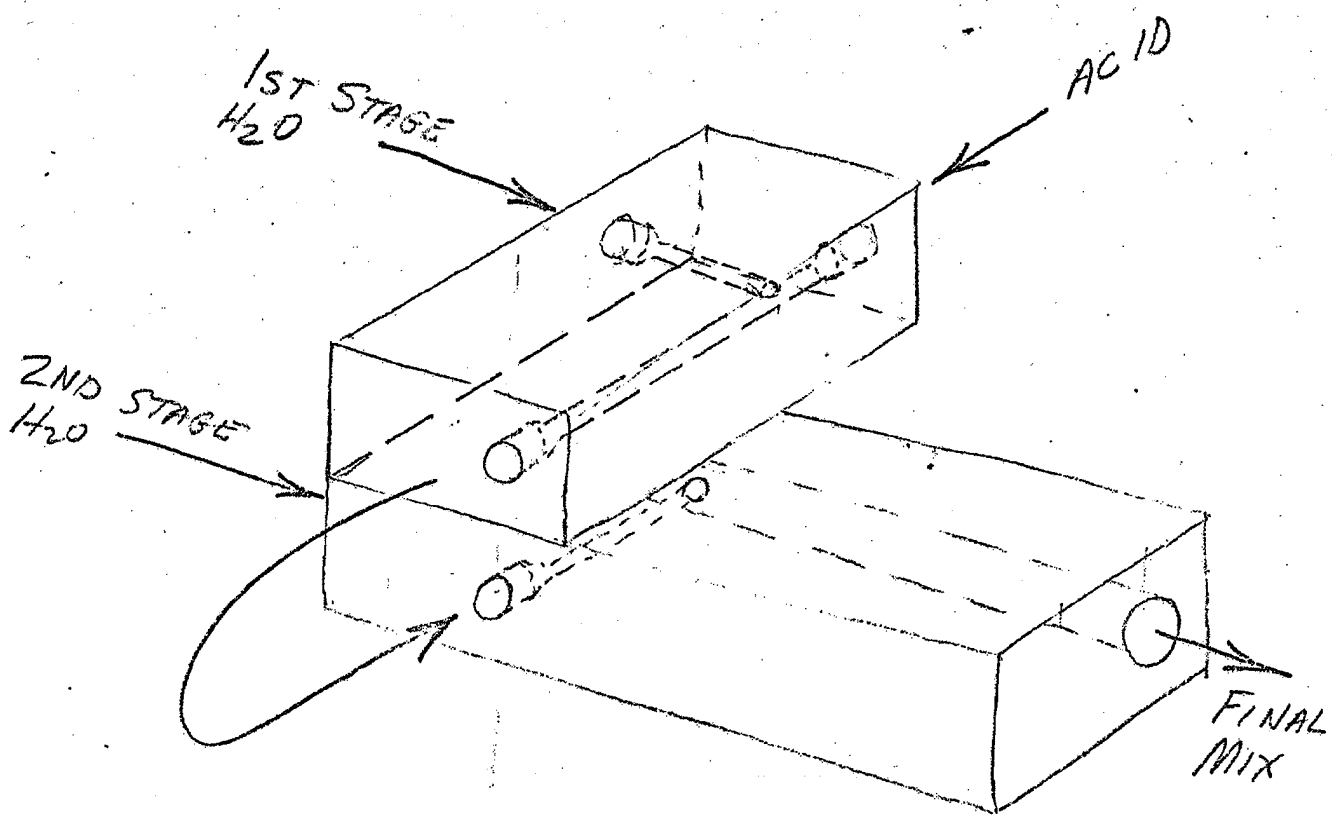
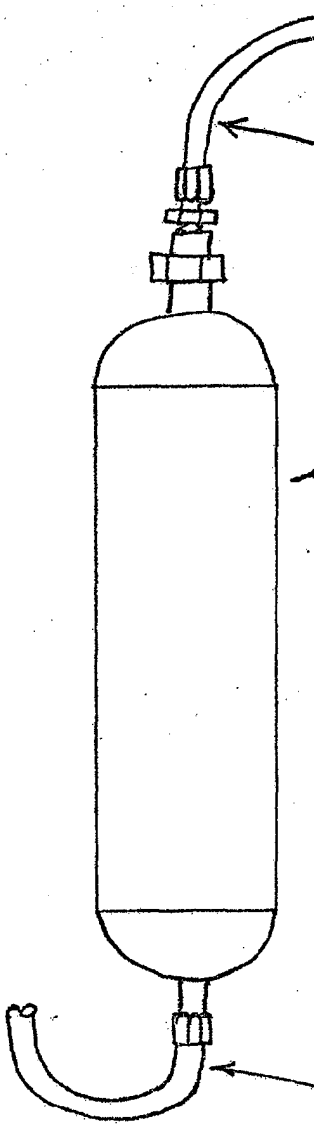
7-1-69



TWO-STAGE MIXER
ASSEMBLY

WLM
7-1-69



½", 20GA. S/S TUBING.

8" SCHED. 80 316 S/S PIPE, 2' LENGTH. WELDED CAPS ON ENDS, DRILLED TO WELD CORRECT FITTINGS TO ADAPT TO 1" UNION (ON TOP) OR TUBING FITTING (ON BOTTOM).

5/8", 18GA. S/S TUBING

BLOWCASES
2 REQ'D.
(REVISED)
WLM 6-25-69

OPERATING PROCEDURE

TWO - STAGE DROWNING UNIT

7 - 23 - 69

1. Open both lab doors leading to safety shower. Check safety shower. Check that Main N_2 shut off valve in hood is open; that N_2 vent is open; and that N_2 pressure gage reads zero.

2. Open acid and water blowcases, carefully. Fill water case. Rod acid case. Add acid not closer than 6" from top. Close blowcases after measuring and taking temperatures.

3. Fill up second stage water tank. Close curtains to hood.

4. Close Main N_2 shut off valve in hood and close the vent over the acid and water blowcases. Check all lines to make sure all the lines are sealed. (See Sketch)

5. The following procedure should be used in turning on the two N_2 cylinders. (Refer to Sketch)

   a. Make sure the vent valve between the Main N_2 flow and Main reducer is closed. Close the auxiliary vent valve and the Brass needle valve.
   b. Open the cylinder valve on the Main N_2 cylinder. (One on the left)
   c. Make sure the regulator valve is open (turn to left until valve moves freely).
   d. Open cylinder valve on the auxiliary N_2 cylinder.
   e. Open the Brass needle valve. One or two turns to the left.
   f. Turn the regulator valve to the right; until the reducer gage reads the correct pressure desired (595 to 605).
   g. Check all lines for leaks.

6. Open Main N_2 shut off valve very slowly allowing pressure to build up slowly. Gas will flow through water flowmeter. (Do not allow surge of gas to slug meter.)

7. Ball valve switch must be closed. Turn on second stage water pump switch.

8. Turn on 1st. stage water, adjust correct reading. (Flow meters)

9. Turn on acid flow. Adjust to correct reading (Flow meters). Readjust 1st. stage water if needed.

10. Note mixer temperature and pressure. When stable, take 1st. stage sample. (About 1/4 of container full).

11. Immediately open second stage water ball valve.

12. Note mixer temperature and pressure.

13. Sample second stage mix. (Fill container.)

14. Immediately shut off acid flow and 1st. stage water flow.

15. Allow second stage water flow to continue for 10-15 seconds.

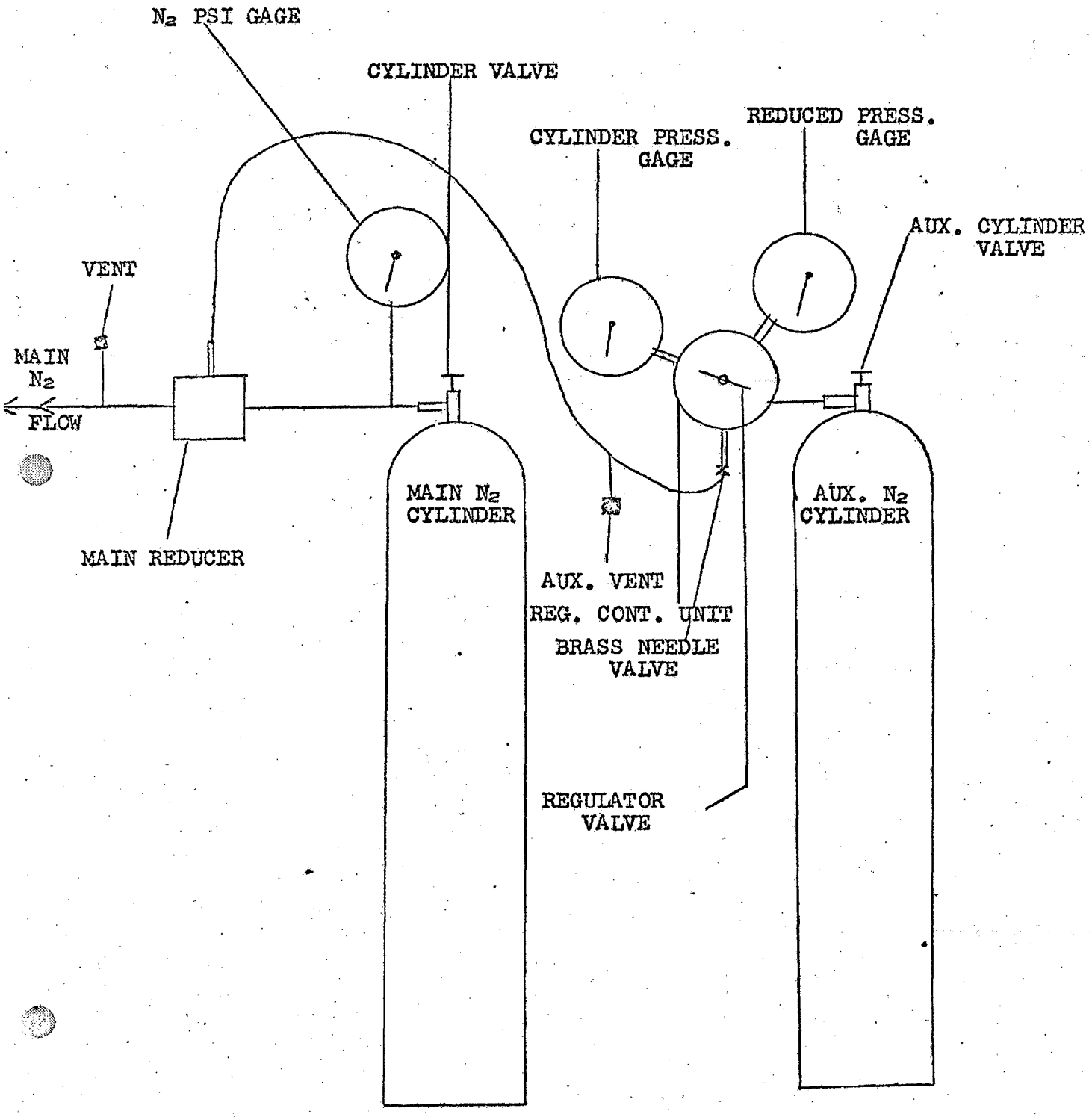
16. Shut off second stage water flow valve and water pump switch.

17. Close Main N_2 shut off valve and open vent over the blowcases.

18. To shut off both cylinders: (See Sketch) Close the cylinder valve on Main N_2 cylinder. (Cylinder on the left). Open the vent between the main reducer and the hood. After this has bleed down--then close the auxiliary vent. This will bleed the left cylinder line. (Check gage.) Now open to the left the regulator valve. This will bleed the auxiliary cylinder discharge line. Close the small Brass needle valve. (Check gages.) Check pressure gage in hood - (Should read zero).

SKETCH

N_2 CYLINDERS



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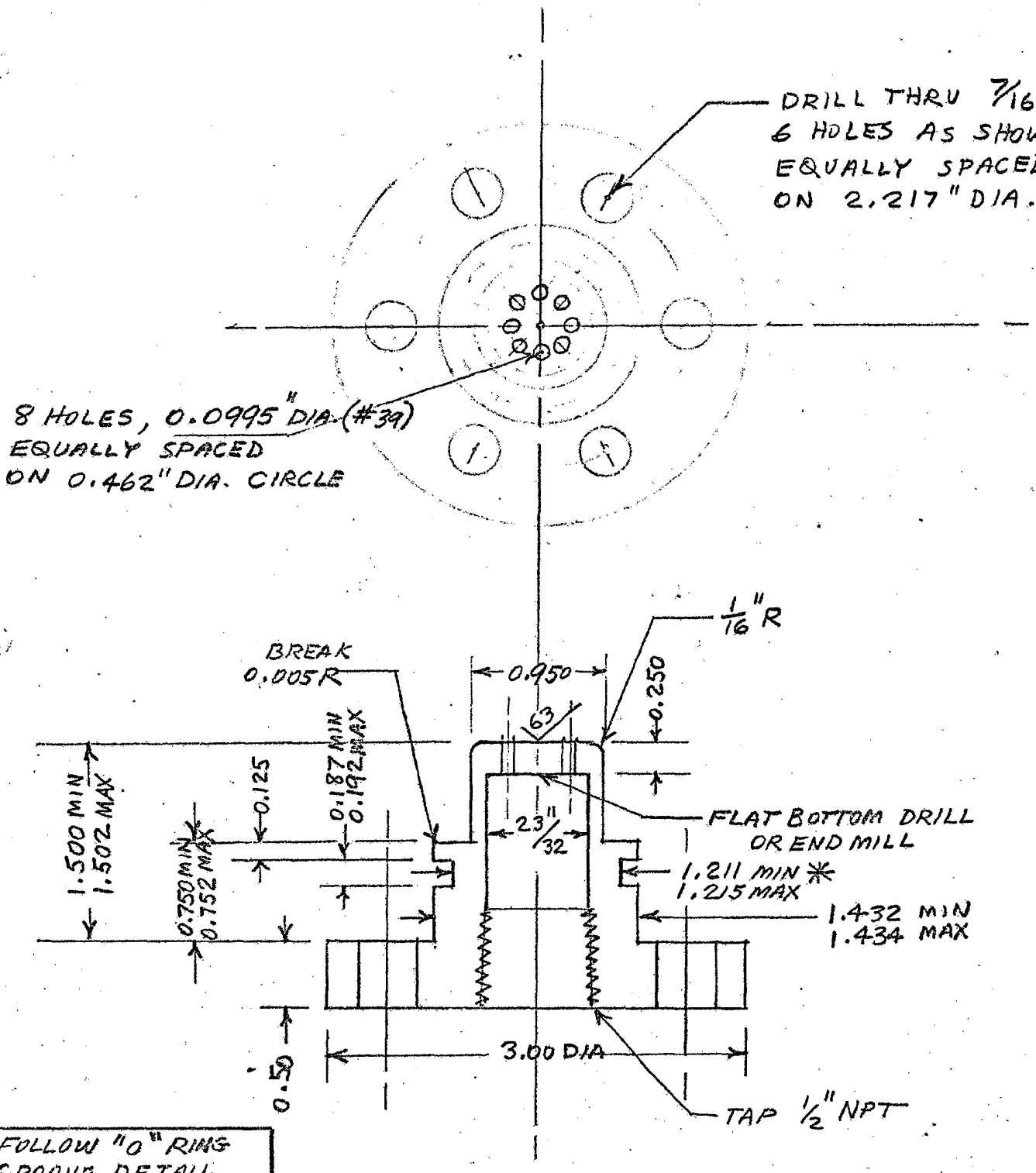
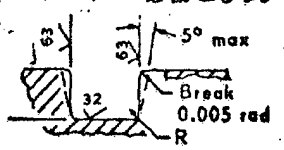


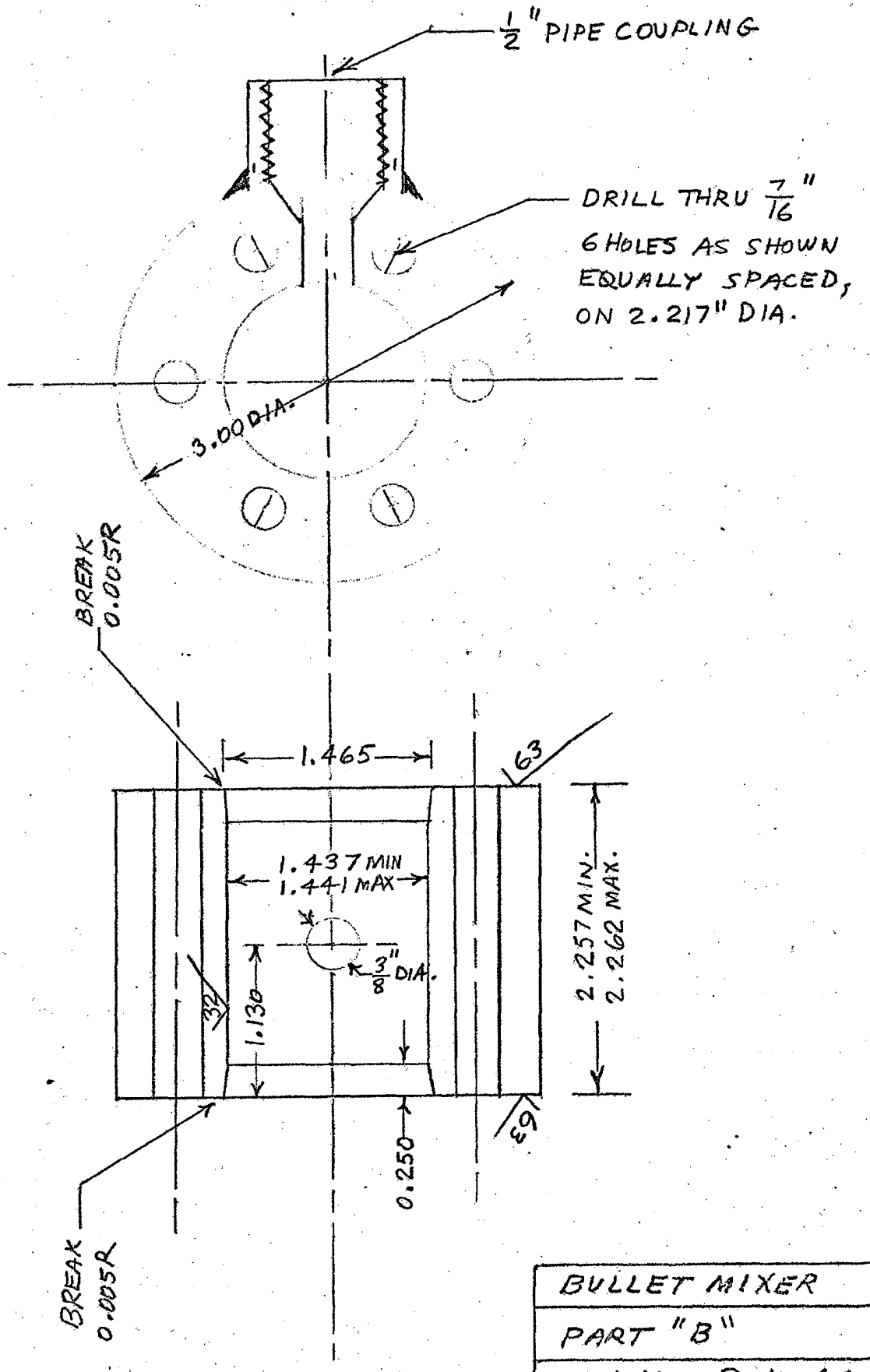
* FOLLOW "O" RING GROOVE DETAIL SHOWN BELOW:



GROOVE DETAIL

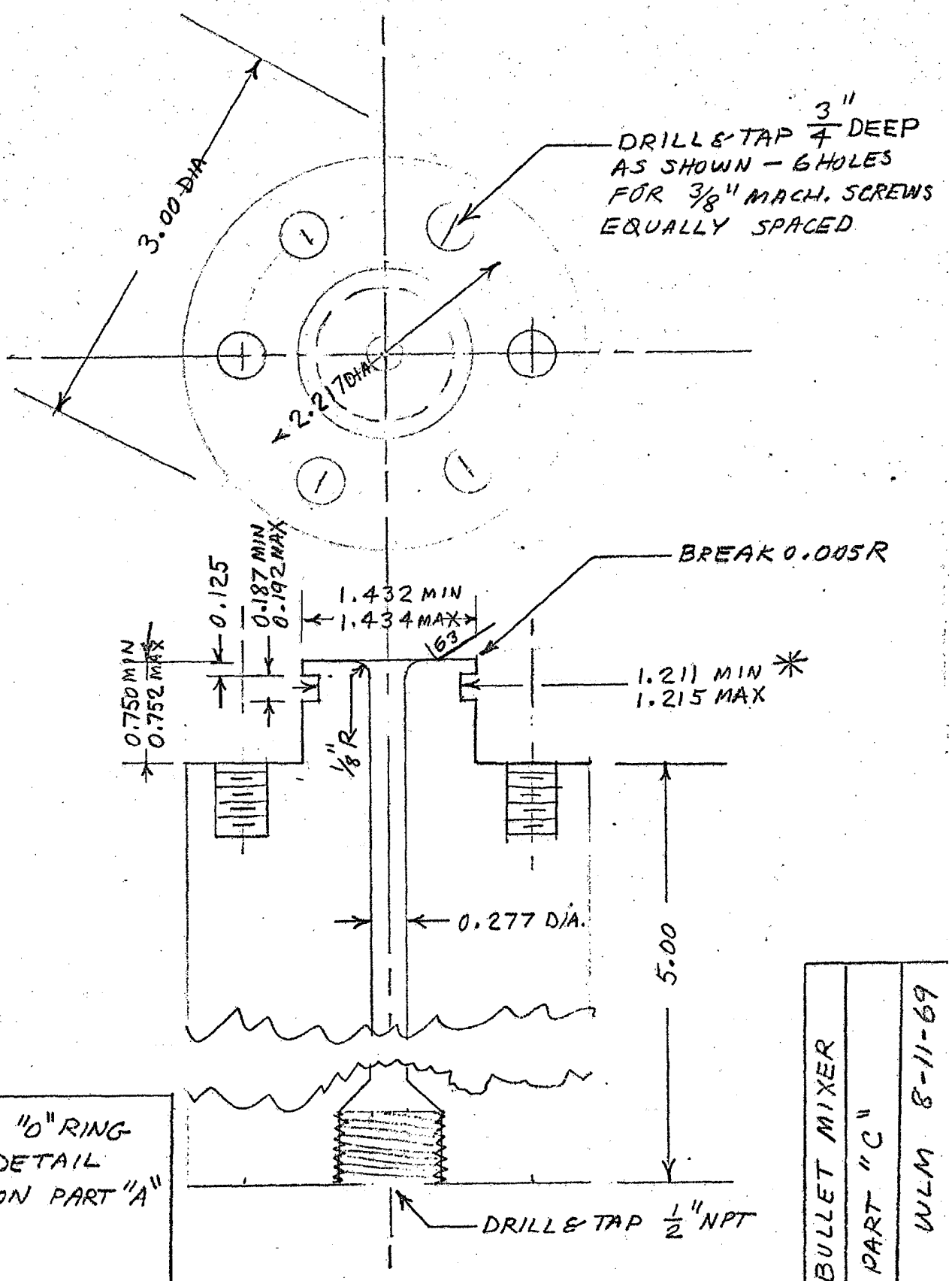
ALL TOL. ±0.003" EXCEPT WHERE SHOWN.

BULLET MIXER
PART "A" - MOD. 1
WLM 8-12-69



BULLET MIXER
PART "B"
WLM 8-11-69

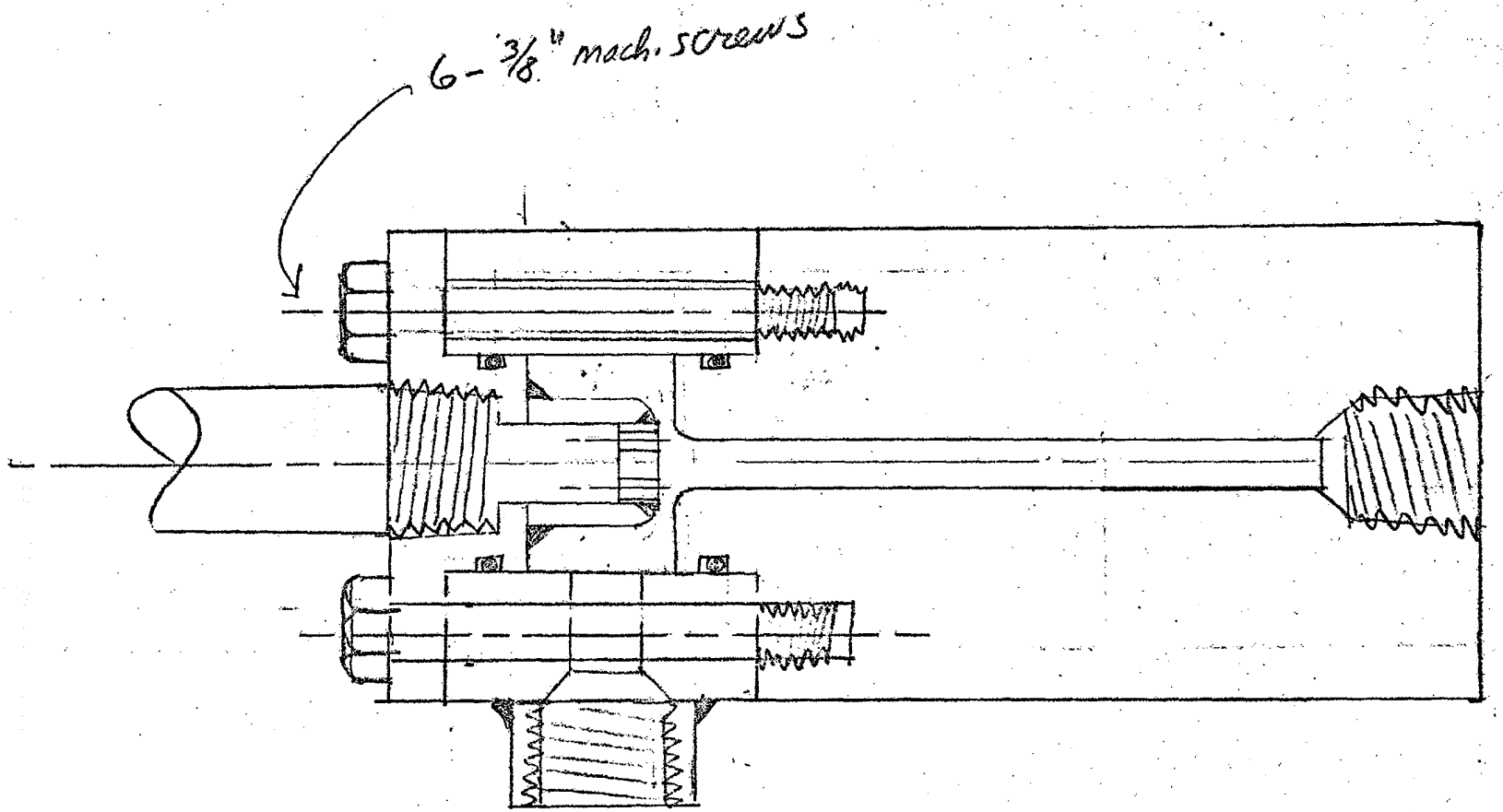
DUP050082183



* FOLLOW "O" RING GROOVE DETAIL SHOWN ON PART "A"

BULLET MIXER
PART "C"
WLM 8-11-69

DUP050082184



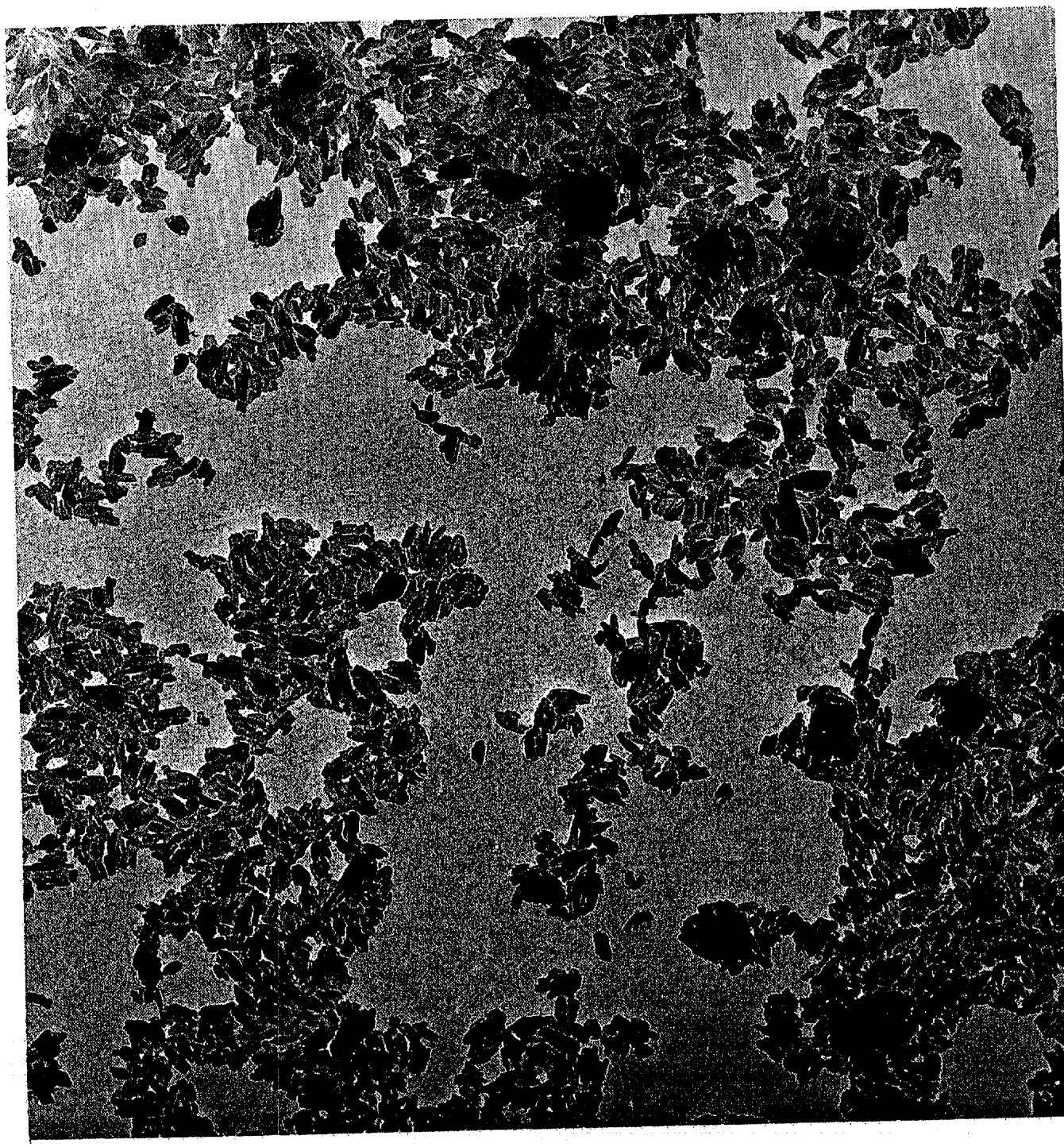
NOT TO SCALE

ASSEMBLY
BULLET MIXER

WLM
8-7-69

DUP050082185

TSD-1



1μ

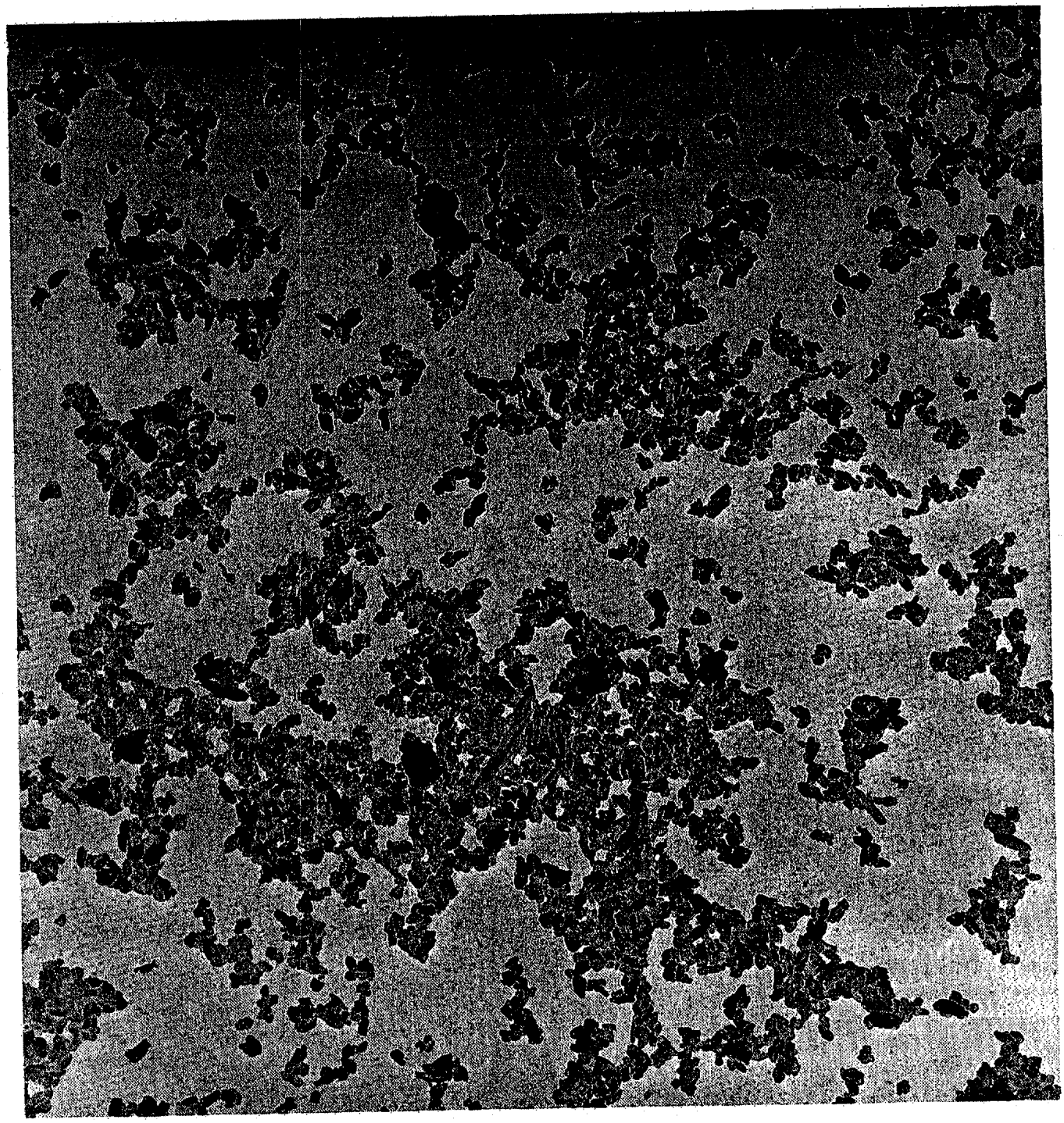
SAMPLE 1886-92A
R.O. INK MAX.

PLATE 6110A MOUNT 6-780 DATE 7-31-69

MAG. 40,000 X

PIGMENTS, NEWARK

TSD-1



1μ

SAMPLE N-623 72481

PLATE 6110E MOUNT 6-781 DATE 7-31-69 MAG. 40,000 X

PIGMENTS, NEWARK

ED IN U.S.A. PHILIPS ELECTRONIC INSTRUMENTS CHART NO. 97096 CHART NO. 20790