FOR DU PONT USE ONLY

Report Number: EX-72-23

Copy Number: 8



Indexed

File: 1865

Distribution on last page

E. I. du Pont de Nemours & Company
F & F, Research & Development Division
Experimental Station Laboratory

Research Report

# FLUSHING OF PIGMENTS



Date Issued:
Period Covered: October, 1971, to May, 1972
Project Number: 211104
Previous Reports: EX-71-33
Notebook Numbers: 567E, 607E

PREPARED BY I. C. Chu

APPROVED BY T. A. Ashe



When this report is no longer needed, please return it to the File Room, F & F Department, Experimental Station.

TABLE OF CONTENTS


| | Page |
|---|---|
| INTRODUCTION | 1 |
| OBJECTIVES | 1 |
| SUMMARY & CONCLUSIONS | 2 |
| ACTION TAKEN OR PROPOSED | 4 |
| PATENT STATUS | 4 |
| PUBLICATION STATUS | 4 |
| ACKNOWLEDGMENTS | 5 |
| DISCUSSION | 6 |
| I. Formulation Guidance - Formulation Guidance Chart | 6 |
| A. General Formulation Guideline | 6 |
| 1. Characterization of Presscake | 6 |
| a. Solids | 6 |
| b. Surface Polarity | 7 |
| c. Surface Charge | 7 |
| 2. Simple "Flushability" Test | 7 |
| 3. Presscakes Directly Flushable into Organic Phases | 8 |
| a. Flushing in B-P Mixer | 8 |
| (1) Charging the Unit | 8 |
| (a) Pigment/Vehicle Ratio and Water Separation Efficiency. | 8 |
| (b) Optimum Working Capacity and Volume of Charge | 9 |
| (2) Mixing Patterns | 11 |
| (a) "Cylindering" | 12 |
| (b) "Riding" | 12 |
| (3) Water "Breakout" and Decantation | 13 |
| (4) Addition of More Resin | 14 |
| (5) Vacuum Stripping of Residual Water | 14 |

TABLE OF CONTENTS (Continued)


| | Page |
|---|---|
| (6) Partial Reduction in B-P Mixer | 16 |
| (7) Final Reduction/"47" Process | 16 |
| 4. Presscakes Requiring Flushing Aids | 17 |
| a. Selection of Flushing Aids | 17 |
| b. Compatibility of Flushing Aid with Vehicle Polymers | 18 |
| (1) Tolerance Limit | 18 |
| (2) Test Method | 19 |
| c. Flushing in B-P Mixer | 19 |
| 5. Criteria for Selection of Candidate Presscakes for Flushing | 20 |
| a. Cost Savings Considerations | 20 |
| (1) High Toner Content Presscakes | 20 |
| (2) Presscakes of High Cost Pigments | 20 |
| (3) Low-Price Presscakes | 20 |
| (4) Presscakes of High Volume Pigments | 20 |
| b. Color Quality Considerations | 21 |
| (1) Particle Size and Size Distribution in Presscakes | 21 |
| (2) Mechanical Grindability | 21 |
| B. Specific Example | 21 |
| 1. Characterization of Presscake | 21 |
| a. Solids | 21 |
| b. Surface Non-Polarity | 22 |
| c. Surface Charge | 22 |
| 2. Simple Flushability Test | 22 |
| 3. Presscakes Directly Flushable into Organic Phases | 22 |
| a. Flushing in B-P Mixer | 22 |
| (1) Charging the Mixer | 22 |

TABLE OF CONTENTS (Continued)


| | Page |
|---|---|
| II. Process Selection and Studies..... | 24 |
| A. Flushing Equipment..... | 24 |
| B. Removal of Residual Water..... | 25 |
| 1. Vacuum Stripping..... | 25 |
| 2. Centrifugation..... | 26 |
| 3. Other Methods..... | 27 |
| C. Reduction..... | 27 |
| D. Preferred Flushing Process..... | 29 |
| III. Evaluation of Flushed Dispersions..... | 29 |
| A. Pigment Range and Scope of Application.... | 29 |
| B. High Spot Cost Estimates..... | 32 |
| 1. In-House Flushed Dispersions vs. Purchased Dispersions..... | 33 |
| 2. Flushed Dispersions vs. 2-Pass "47" Process Dispersions..... | 34 |
| 3. Summary..... | 35 |
| REFERENCES..... | 37 |
| TABLES I - VI..... | 38-45 |
| FIGURE 1..... | 46 |
| APPENDICES I - IV..... | 47-55 |
| ABSTRACT..... | 56 |
| DISTRIBUTION LIST..... | 57 |


ICC/ayk
6/28/72

## INTRODUCTION

The term "Pigment Flushing" refers to the direct transfer of water-wet presscakes from an aqueous into an organic phase. Potential advantages of "flushing" lie in the facts that (a) it circumvents the oven drying step in the pigment manufacturing which causes formation of agglomerates, (b) the less aggregated pigment particles will be easier to grind and contribute to better dispersion quality, and (c) the presscakes, in many cases, contain higher toner content which constitutes a basis for cost savings - particularly for the expensive pigments.

The flushing process consists basically of two operations --- (a) transfer of pigment particles into the organic phase and (b) removal of all residual water. In addition, if the presscakes are too hydrophilic, they prefer to remain in the water phase. Under such circumstances, a proper flushing aid has to be selected to affect the flushing. The dispersion quality of flushed bases depends heavily on the presscake quality (i.e., the particle size distribution in the presscake). For presscakes which already contain significant amounts of loose agglomerates, following the "flushing," a reduction operation (such as sand grinding, roll milling, etc.) would be needed to ensure optimum quality.

In the previous report (EX-71-33), we dealt, in some detail, with the general flushing technology. The topics of (a) presscake flushability, (b) selection of flushing aids, (c) particle size and size distribution, and (d) illustrative applications were included.

This report will cover a consolidated and preferred flushing process, formulation guidance, in detail, for flushed dispersions, scope of application, and a high spot cost study.

## OBJECTIVES

The overall objective is to assess the potential of "flushing" for F & F as an alternative way to manufacturing pigment dispersions.

The technical objectives are to define a flushing process, to provide a general formulation guidance, to establish the incentives of "flushing" in terms of cost and quality, to demonstrate scope of application, and finally the feasibility of commercialization.

SUMMARY & CONCLUSIONS

- A "Preferred Flushing Process" has evolved from the studies of efficiencies of the various unit operations required to convert a presscake into a usable flushed dispersion for organic vehicles. The preferred flushing procedure consists primarily of (a) transferring the presscake into the organic vehicle in a Baker-Perkins (B-P) Flusher, (b) vacuum stripping the trapped residual water using a B-P flusher with an air tight lid, heat jacket, and condensing equipment, (c) partial reduction in B-P flusher, and (d) final reduction with a "47" process sand mill.

The above process would, in most cases, provide adequate dispersion quality.

Super centrifugation may be used optionally in addition to the above process to further improve the dispersion quality and provide special effect of color and styling if needed.

- A "Formulation Guidance Chart" which gives step-by-step instructions for processing the presscake and formulating a flushed dispersion has been prepared.

Also included in the "Formulation Guidance Chart" are (a) methods of characterization of presscakes and illustration of their relations to the flushing behaviors and flushing processes and (b) criteria for selection of candidate presscakes for flushing from the standpoints of economics as well as the dispersion quality.

- A limited range of pigments have been investigated and their suitability for flushing and scope of application in various product lines established.

| | | |
|---|---|---|
| Inorganic Pigments: | Hydrous iron oxide (Harmon) and Transoxide yellow (W-682, Hilton-Davis) | |
| Organic Pigments: | Copper phthalocyanines: | W-765, W-764, B-C-1p |
| | Quinacridones: | W-839, W-819, W-811 |
| | Irgazine yellow: | 2RLT |
| | Thiofast: | W-312 |
| Others: | PVF Dispersion for Coil Coating | |

Of these, the Irgazine yellow and Hydrous iron oxide (Harmon) showed no advantages as a result of flushing due to the large

crystals already existing in the presscakes and W-811 in the Centari® vehicle due to the opaque grade and large particle size in the presscakes. The remaining pigments were evaluated preliminarily in the following product lines and showed promises either economically and/or quality-wise: (a) Centari® refinish enamels (931 line), (b) Acrylic refinishes (946 line), (c) Powder coating, (d) PVF Coil coating, and (e) Dulux® (195 line).

- In-depth evaluations of the flushed dispersion of selected test pigments (W-682 and W-839) in LDL and Centari® systems were made at Flint R & D Laboratory: (a) Flushed W-839 dispersion for Centari® showed good color, viscosity, and settling stability, and significantly greater tinting strength. Gloss, hardness, and gasoline resistance were adequate; and the dispersion was shadable to meet the color specifications of existing products. (b) Flushed W-682 for Centari® showed better two-tone quality and cleaner yellow color without the undesirable red side-tone. (c) Flushed W-682 for the LDL was flocculated in the letdown and gave poor two-tone quality.

- PVF pulp can be flushed successfully into organic solvent (propylene carbonate) using 0.5% transfer agent [Bis (2EH)hydrogen phosphate]. Flushed PVF dispersion exhibited better coalescence and tougher and glossier film which were attributed to the better dispersion and finer particle size of the flushed enamel. Eight colors have been formulated from the flushed PVF and panels are now undergoing exposure tests.

- A high spot cost study indicates that the major cost item of a mill base is the toner cost. The costs of in-house flushed dispersions are considerably lower (~ $2.00-5.00/lb. pigment) than those of purchased dispersions and moderately lower (~ $0.90-1.00/lb. pigment) than the 2-pass "47" process dispersions if there is an increase of tinting strength in flushed dispersion (or a favorable price differential for the presscakes) amounting to a net dollar value of ~ $1.00/lb. on dry basis.

In conclusion, we feel that the "flushing process" will provide F & F with an added dimension of Dispersion-Manufacturing. "Flushing" should be implemented on a selective basis - some pigments will definitely give beneficial results if flushed; others will make insignificant difference. The flushing technology, once instituted at a given plant site, may receive considerations as an alternative way of

making pigment dispersion along with the other methods (such as sand, ball, and 2-roll milling) and should be used for those cases and pigments to cash in the quality advantages and cost savings available only through "flushing."

ACTION TAKEN OR PROPOSED

The overall status of "Pigment Flushing" has been reviewed with refinish marketing. A forecast of pigment candidates suitable for formulation and alignment of flushed dispersions was compiled. General formulation guidance and specific examples were provided.

Process Chemistry will demonstrate the flushing process in the existing semi-works equipment at Parlin (i.e., W & P mixer) and obtain a more precise picture of the manufacturing cost.

Exploratory will assist the scale-up work in a consulting capacity, if necessary.

PATENT STATUS

Prior art has been discussed in previous report, EX-71-33.

FFD-3234, "Flushed Dispersions and Process for Manufacturing Same," based on mixing flushing/centrifugation process was submitted to Patents & Contracts Section (11/1/71). The case has not yet been filed.

A patent proposal on the preparation of PVF coil coating enamels via flushing process will be initiated jointly with Mike Miller, Marshall Laboratory, if the results of the accelerated exposure tests (now underway) are promising.

PUBLICATION STATUS

We do not contemplate to publish the results contained in this report at the present time.

ACKNOWLEDGMENTS

Acknowledgments are due to J. G. King, G. W. Orvis, J. L. Evans, and M. H. King of Flint R & D Laboratory; Mike Miller and R. D. Anderson of Marshall Laboratory; F. Rohrbacher and L. R. Harper of Experimental Station Laboratory for their assistance in evaluating the flushed dispersions in the various product lines.

I am appreciative of the helpful discussions and suggestions of D. Wittman, J. R. Moffett, and E. J. Donnelly of Marshall Laboratory, W. Kosachuk of Parlin Plant Laboratory; and H. L. Jakubauskas of Experimental Station Laboratory.

A special note of appreciation to Sam Speakman who made the arrangements for the installation of the Laboratory Baker-Perkins Flusher in the equipment area of Building 174 and assisted in drafting up the operation procedure and safety practice.

The laboratory work was skillfully performed by Tom M. Warner, Charles R. Fritz, Bob E. Brumbaugh, and Bob G. Burgess.

## DISCUSSION

### I. FORMULATION GUIDANCE - FORMULATION GUIDANCE CHART

Making a pigment dispersion via the flushing route consists of three basic processing steps:

(1) Transfer of pigment particles from a water wet presscake into an organic phase

(2) Removal of $H_2O$

(3) Reduction to paint consistency.

In the current preferred process (see Section II-C), operations (1) and (2) are both carried out in a heavy duty Baker-Perkins mixer. Following the "water removal" step, a partial reduction is made in the Baker-Perkins mixer to lower the consistency of the mixture to a level so it can easily be emptied from the mixer. The final reduction is made in a "47" process continuous sand mill in order to break up the loose agglomerates originally present in the presscake and the small lumps formed around the wall of the container and near the mixing blades during the vacuum stripping operation.

#### A. General Formulation Guideline

A step-by-step formulation chart is shown in Table I. This chart will provide a general guideline for formulating a flushed dispersion suitable for paint uses from a presscake. Each formulating and processing step (as marked and numbered in the chart) will be further illustrated and explained with examples and details in the next sections of this report.

##### 1. Characterization of Presscake

###### a. Solids

The percent solids of presscakes vary widely from 20-50% depending on the hydrophilic nature of the presscakes. The average solids of a given presscake is usually provided by the vendor on the shipping paper and on the identification label.

One should be aware that the presscake is not a perfectly uniform material. In experiments where reliable solids must be used, it is suggested that an average solids based on 5 or more determinations (of samples taken from different areas and depths) should be used.

Precautions which tend to minimize the variation in solids are:

- Use up all presscake once the seal is open
- Sample the presscake at the time it is being used, determine the average solids, and use the experimentally established solids in all computations; this procedure will be necessary in experiments in which the advantage of increased tinting strength of the flushed dispersion has to be established.

b. Surface Polarity

Whether a presscake can be transferred from an aqueous into an organic phase is decided by the free energy change accompanying the transfer process. A negative free energy change will result in a successful transfer and vice versa. The flushability of a presscake can also be conveniently correlated with surface non-polarity. In previous work (EX-71-33), we have shown that a pigment with > 70% surface non-polarity will spontaneously flush into the organic phase; while a pigment with < 60% surface non-polarity will remain in the aqueous phase.

The experimental procedure for obtaining the surface non-polarity of presscakes has been described in detail in EX-71-33.

c. Surface Charge

In case a presscake will not spontaneously flush into an organic phase (solvent or resin), the knowledge of its surface charge (+ or -) will assist us to select the types of flushing aids required to effect the flushing.

Experimental methods for determining the pigment surface charge and examples of selection of flushing aids were given in EX-71-33. Additional examples and compatibility considerations will be presented in a later section of this report (section I-A-3).

2. Simple "Flushability" Test

While the flushability of a given presscake is governed by and can be predicted from the inherent surface property (i.e., surface non-polarity) of the pigment as described in the earlier sections (section 1-b), a simple and

quick test would be desired for the convenience of practical formulation.

The following "flushability" test has often been used in our work and proven satisfactory.

The test involved weighing out 100 g. of presscake (dry basis) in a 16 oz. wide mouth jar. To this was added 100 g. of the organic vehicle into which the presscake was to be flushed. The mixture was then stirred with an air driven stirrer for 10 minutes. "Flushing" had occurred if one of the following phenomenon was observed:

- $H_2O$ was separated into a distinctive phase
- A homogeneous mixture was formed which was of significantly lower consistency than the original presscake; furthermore, the color component of this mixture was miscible with toluene but immiscible with $H_2O$.

Presscakes which failed to flush over into the organic phase would respond to the "toluene"/"$H_2O$" test in an opposite way.

This test would divide quickly the presscakes into two categories: (1) those that can be flushed directly into an organic phase and (2) those that will require flushing aids. They will be dealt with separately in sections 3 and 4.

## 3. Presscakes Directly Flushable into Organic Phases

### a. Flushing in B-P Mixer

#### (1) Charging the Unit (i.e., B-P Mixer)

##### (a) Pigment/Vehicle Ratio and Water Separation Efficiency

The relationship between the presscake/vehicle ratio and $H_2O$ separation efficiency is shown in Table II. The amount of decantable $H_2O$ increases with increasing "presscake/vehicle" ratio and begins to level off at 50/50 presscake/vehicle ratio. Table IIa showed parallel results if the organic phase was a pure solvent (i.e., toluene).

Based on these results, a presscake (dry weight)/ organic vehicle ratio in the range of 50/50 to 60/40 is

recommended as a desired composition for the initial and subsequent charges.

### (b) Optimum Working Capacity and Volume of Charge

The working capacity of a given B-P mixer is indicated on the specification sheet by the manufacturer. In order to utilize the full working capacity of the unit, it is a general practice to divide up the total charge into several portions and load the mixer to capacity in several steps. This practice is necessary because the presscakes contain 50-80% water. The water present in the initial charge occupies a significant portion of the mixer volume. With the 1st $H_2O$ decantation, the volume of the initial charge will shrink. The 2nd charge may then be added to bring the sample volume closer to the theoretical mixer capacity. Another advantage of the multiple charging procedure is that it allows more water to be decanted.

We recommend that the total volume of the initial charge be in the range of 70-90% of the theoretical working capacity of B-P mixer. After the 1st $H_2O$ decantation, a subsequent charge of about equal volume to that of the decanted $H_2O$ may be added to the mixer so that the combined volume of the two charges be kept within the recommended range. Outside this range, the following situations may arise:

- Inefficient mixing, if < 70%
- Inadequate room for partial reduction (which reduces the consistency of flushed dispersion and facilitates emptying from B-P mixer (see section 3-a-9); if >90%.

The specific volume of a given presscake may be calculated from its percent solids and the gallon weight (or specific gravity) of the dry pigment by the following formula:

$$V_{p.c.} = \frac{a}{(GW)_p} + \frac{1-a}{(GW)_w} \qquad (I)$$

Where $V_{p.c.}$ = Specific volume of presscake (gallon/lb.)
$(GW)_p$ = Gallon weight of dry pigment (lb./gallon)
$(GW)_w$ = Gallon weight of water (~ 8.32 lbs. at room temperature)
$a$ = % solids of the presscake

The specific volume ($V_{resin}$) of a given resin (in gallon/lb.) is equal to the reciprocal of its gallon weight - a quantity usually specified on the formulation card of the resin.

A working example for calculation of the initial charge is given below:

**Problem** Calculate the composition and the total amount of the initial charge required to fill up 75% of the working capacity of the B-P mixer assuming (1) B-P mixer has a working capacity of 2.25 gallon, (2) the gallon weight of the pigment in the press-cake is 28.2 (lb./gal.), (3) the gallon weight of the organic resin is 7.8, (4) the solids % of the presscake is 38%, and (5) the weight ratio of presscake (dry basis)/resin is to be maintained at ~ 55/45.

**Solution** The specific volumes of the presscake and the resin can be calculated from the available information:

$$\text{Specific Volume of Presscake } (V_{p.c.}) = \frac{0.38}{28.2} + \frac{0.62}{8.32}$$
$$= 0.0135 + 0.0745$$
$$= 0.088 \text{ gallon/lb.}$$

Let $\underline{x}$ and $\underline{y}$ respectively represent the number of lbs. of presscake and resin required in the initial charge.

The values of x and y can be obtained by solving the following equations:

$$\begin{cases} \frac{(x)(a)}{y} = R & \text{----------(1)} \\ x(V_{p.c.}) + y(V_{resin}) = 0.75\ V_m & \text{----------(2)} \end{cases}$$

Where R = presscake (dry basis)/resin (weight ratio)

$V_{mixer}$ = working capacity of the mixer

Substituting the values of a(= 0.38), $V_{p.c.}$(= 0.088), $V_{resin}$ (= 0.128), R(= 55/45), and $V_{mixer}$(= 2.25 gal.), we get:

$$\begin{cases} y = (0.38)\frac{45}{55}x = 0.31x & \text{----------(1a)} \\ 0.088x + 0.128y = 1.69 & \text{----------(2a)} \end{cases}$$

From (1a) and (2a), the quantities (lbs.) of presscake and resin to be loaded in the initial charge are:

$x = 13.20$ lbs.

$y = 4.14$ lbs.

The same procedure may be used to calculate the quantities of presscake and resin in the second charge if the volume made available by the 1st $H_2O$ decantation is known or can be estimated (from a smaller scale run).

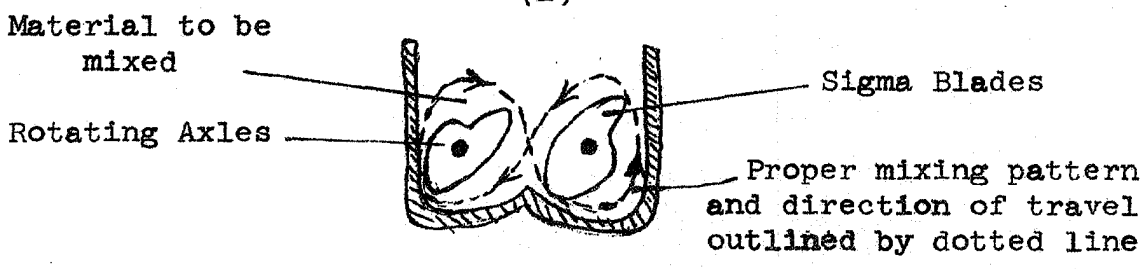
## (2) Mixing Patterns

The optimum presscake/resin ratio and volumes of initial and second charges discussed in the preceding section are set in a range so that an effective mixing pattern (among other things) may be obtained.

In this section, we attempt to give an account, in qualitative terms, of the elements which constitute an effective mixing pattern and how to correct the poor mixing patterns.

The blades in a double-arm Baker-Perkins type mixer are driven at differential speeds at a pre-set clearance (~ 15 mils) against the wall of the container. In a proper mood of mixing, the material should be forced through the narrow clearance continuously and kneaded between the two blades thoroughly. A small amount of material sticking to the back side of the sigma blade tends to stay out of circulation. To eliminate this phenomenon completely would be difficult. A proper mixing action, however, may minimize it. Under proper mixing action, an element of the material in the mixture would travel a path as traced out schematically by the dotted line in the drawing.

(1)



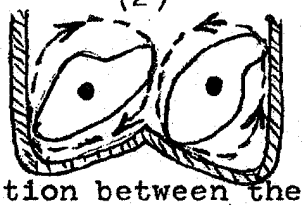

With some experience, one can easily recognize the above pattern of mixing.

Two of the commonly encountered poor mixing patterns are illustrated below:

(a) "Cylindering"

"Cylindering" refers to the phenomenon that the mixture stays and moves along with the individual blade; there is

(2)



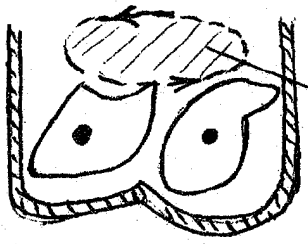
very little kneading action between the blades, and the material does not get circulated. "Cylindering" occurred frequently during the "reduction" stage when resin (or solvent) was added too hastily to a highly viscous and somewhat stiff mass. The added resin would lubricate the surface of the mass and break up the continuous mixing pattern [i.e., Drawing (1)].

All attempts should be made to prevent this from happening (see "Reduction," Section 3-A-9).

Once "cylindering" takes place, the corrective measure would involve (i) shutting off the mixer, (ii) cutting through and breaking off a piece of the highly viscous and stiff mass, (iii) replacing the piece between the two blades, and (iv) restarting the machine. This sequence of operations has to be repeated until the normal mixing pattern is resumed.

(b) "Riding"

(3)



Material to be mixed riding on top of the blades

"Riding" refers to the phenomenon that a significant portion of the material to be mixed rides on top of the moving blades as illustrated in the drawing. The material inside the "riding" mass would stay un-mixed.

"Riding" occurs when the material to be mixed has a strong coherence and weak adherence to the blades.

The preventative measure is to lower the overall consistency of the mixture in the formulation.

The corrective measure, after it has happened, would be similar to that recommended for the remedy of "cylindering." Here the "riding" mass must be broken up into smaller pieces and repositioned in the mixer.

In addition to the two distinctive patterns stated above, poor mixing efficiency may result from low mixture consistency. In this case, the blades would move gently through the relatively fluid mixture without causing much agitation. As an example, flushed dispersion in the final stage of reduc- to paint consistency (i.e., 1000-2000 cp.) would be too fluid to be mixed effectively by the B-P type mixer.

(3) Water "Breakout" and Decantation

Water "breakout" refers to the phenomenon that after the pigment particles being flushed over into the organic phase water separates and forms a distinct phase. The B-P mixer has a distinct phase. The B-P mixer has a device which allows the mixer to be tilted to the horizontal position thus decanting the separated $H_2O$ phase into a receiver or the floor drain.

The ease of water "breakout" varies from pigment to pigment. For instance, the presscake of W-765 (Monastral® Green) would show signs of "breakout" in just a few minutes after being mixed with the organic phase (i.e., toluene or RC-3346), while the presscake of W-839 (Monastral® Violet) would not give a clear cut $H_2O$ "breakout" after an hour of mixing. The difference in $H_2O$ "breakout" behavior between these two pigments can be explained in terms of their surface non-polarities. The data shown below are taken from our earlier report (Table II, EX-71-33):

| Pigment | % Non-Polarity | Free Energy of Flushing (Ergs/cm.$^2$) |
|---|---|---|
| W-839 | 75 | -15.2 |
| W-765 | 85 | -30.1 |

It is to be noted that while both pigments have negative free energy of flushing and a high enough surface non-polarity (> 70% non-polarity) to be flushed into the

organic phase, there is a difference in magnitude of the free energy change accompanying the flushing process and in degree of surface non-polairty. This difference is reflected in the "ease of water breakout." The partial affinity of W-839 to water gives rise to a meta-stable dispersed system and prevents the presscake water from coalescing into a bulk distinct phase which is required for decantation. The case of W-839 is probably typical of many other presscakes whose surface characteristics fall into the general category as that of W-839. Under such circumstances, we would advise increasing the temperature of the flushing mixture. Higher temperature tends to destabilize the "$H_2O$/organic" dispersed system and promote coalescence.

In the specific example of W-839, water "breakout" was brought about and decantation made possible when the temperature was increased to 60-70°C.

(4) Addition of More Resin

After the final water decantation, it is suggested that more resin be added to bring the resin solids/pigment (dry basis) weight ratio to the neighborhood of 40/60 or greater. At this ratio, generally, there will be enough polymer present to make a stir-in pigment, if all the pigment particles are uniformly coated with the polymer. In our experience, this practice would better preserve the presscake quality and increase the ease of "reduction."

(5) Vacuum Stripping of Residual Water

The amount of residual water remaining in the flushed dispersion (after decantation) can be estimated from the following relationship:

$$W_r = (W_{p.c.}) \times (1-a) - W_d \qquad (3)$$

Where $W_r$ = Residual $H_2O$ (weight unit)
$W_{p.c.}$ = Total charge of presscake (weight unit)
$a$ = % solids of presscake
$W_d$ = Total amount of $H_2O$ decanted (weight unit)

This residual water has to be removed by vacuum stripping. Usually the organic liquid components in the resin (such as toluene or acetone, etc.) form azeotropes with water and allow water to be removed readily at moderate temperatures (50-80°C) with house vacuum (20"-25" Hg).

(i) When the B-P mixer is equipped with a condenser, the completion of water removal may be detected by sampling the condensate at 15 minutes intervals during the stripping operation.

- If the condensate contains a separate water layer or appears milky, it is an indication that a significant amount of $H_2O$ is still present in the mixture.
- If the condensate is clear, it indicates that water removal is near completion. An additional 15 minutes of stripping would ensure complete water removal from the flushed dispersion.

(ii) If the flusher unit is not conveniently equipped with a condenser as is the case for many smaller laboratory B-P mixers, the end point of complete $H_2O$ removal can reasonably be assured by one of the following procedures:

- Microscopic Method: Presence of residual $H_2O$ can easily be observed as distinct water droplets with an optical microscope ($\sim$ 100-200X). Samples are to be taken from the flusher unit at appropriate intervals and examined under the microscope to establish the end point.
- Rate of Total Condensation: First, one must establish the average rate of total condensation (i.e., water and toluene) under standardized vacuum stripping conditions (i.e., 25" Hg and 50°C with $N_2$ purge). If toluene is being used as a primary azeotrope liquid, one can safely assume that all residual $H_2O$ would be gone when the total condensation is equal to 3 times the estimated amount of residual $H_2O$ [equation (3)].

[Example: In the 2½ gallon B-P mixer, the average rate of total condensation is about 20 g./min. (at 24-25" Hg; 50°C). Assume the residual $H_2O$ to be vacuum removed is 1000 g., this would require, by the above rule of thumb,

$$\frac{3 \times 1000}{20} = 150 \text{ min. (or 2.5 hours)},$$

2.5 hours of vacuum operation.]

In order to maintain an effective mixing pattern and approximately a constant mixture consistency throughout the vacuum stripping operation, solvent (i.e., toluene) has to be added to compensate for the loss in the total condensate. As a rule of thumb, 2 $W_r$ [see equation (3)] of solvent is to be

added in several portions to the flusher unit in equal intervals throughout the vacuum operation period. This practice is to prevent the mixture from being unduely stiff and tough which could overload the motor and adversely affect the ease of reduction (see section 3-a-6).

(6) Partial Reduction in B-P Mixer

A partial reduction with solvent and/or resin follows the vacuum stripping. At the completion of vacuum stripping, the material usually is too thick to be poured freely out of the mixer. A partial reduction brings the consistency to a pourable state and facilitates the emptying of the flushed dispersion from the mixer.

Addition of resin (or solvent) must be made slowly in small portions at the beginning. Each successive portion is to be added after the previous portion has been thoroughly mixed in (to avoid "cylindering" phenomenon). As the overall consistency has been reduced to a partially pourable state, bigger portions may be added since the resin can now be mixed in more readily. Partial reduction in B-P mixer may take 30 minutes to more than 2 hours depending on the initial consistency of the mass.

Build-up of lumpy material on the mixing blades is an indication of hasty reduction (particularly at the beginning stage). It can be minimized by decreasing the amount each added portion and/or increasing the time interval between each addition.

The partially reduced dispersion is to be emptied from the B-P mixer into a storage and pre-mix tank (for the final reduction with "47" process). The residual dispersion in the B-P mixer should be rinsed off with solvents, recovered, and blended with the rest of the batch.

(7) Final Reduction/"47" Process

The final reduction consists of a single pass through the continuous sand mill ("47" process). This procedure was selected over many other alternatives on the basis of the superior dispersion quality it offers and of the fact that it permits greater flexibility and less critical formulating practice in the "partial reduction" and many other previous operations (such as optimum resin/pigment ratio, etc.).

Here the partially reduced dispersion is further reduced with solvent/resin to a viscosity range suitable for sand grinding (~ 800-1500 cp.). Our results indicated that a single pass (at 30-60 GHP in 8 gallon unit) would be sufficient to smooth out most of the loose agglomerates frequently found in the partially reduced stock.

### 4. Presscakes Requiring Flushing Aids

Presscakes having a high surface polarity (EX-71-33) would remain in the aqueous phase when mixed with organic liquids or resins. Formulating a flushed dispersion from one of these presscakes, in addition to the procedures and considerations detailed in the preceding section (i.e., section 3), one has to (a) select an effective flushing aid and (b) test its compatibility with the vehicles and the solvent system in the end product.

#### a. Selection of Flushing Aids

An effective flushing aid serves two basic functions:

- Adsorbs strongly on the pigment surface
- Provides high affinity to the organic phase.

These functions can best be fulfilled by surfaced active molecules in which the hydrophilic head would interact with pigment particles in the aqueous phase and the hydrophobic tail would provide the needed organic affinity.

The following are offered as a general guideline for initial screening and selection of flushing aids.

- Surface Charge of Presscake and Ionic Type of Flushing Aids

A precise knowledge of the surface composition of the pigment would always help in selecting the type of flushing aids to be used. But such information is not always available.

The surface charge of presscakes in aqueous phase can readily be determined (EX-71-33) by Zeta meter techniques. If the surface charge of the presscake concerned is known (say, for instance, positive), surface active agents of the opposite ionic type (i.e., anionic) would be good candidates for initial screening. The opposite charge effect promotes interaction and adsorption. (It is to be noted that the adsorption phenomenon can be very specific to the physical and chemical nature of the

species involved. In the above illustration, one may find several anionic types which would assist pigment flushing, but one type would frequently turn out to be more effective than another. Examples are alkyl phosphates vs. long chain carboxylic acids to an iron oxide yellow presscake - W-682. The alkyl phosphates are significantly more effective as a flushing aid.)

- Water Insolubility of Flushing Aids

Water soluble surfactants are seldom effective flushing aids. Table IV shows the experimental evidences to this effect.

Water solubility (or insolubility) data of surface active materials are sometimes listed in the technical information sheets prepared by the manufacturers.

Should the manufacturers give the HLB values for their surface active materials (as some of them now do), water insolubility would correspond to a low HLB value in the range 1.0-6.0.

For additional illustrations concerning the topic of "Flushing Aid Selection," the reader is referred to EX-71-33 (p. 10-15).

b. Compatibility of Flushing Aid with Vehicle Polymers

(1) Tolerance Limit

True compatibility between polymeric components and additives (blended in all proportions) is rare. Moderately compatible pairs, however, can be blended up to a certain weight ratio without noticeable detrimental effect.

The tolerance limit of a given flushing aid with the vehicles in the end product, in so far as its effect on dispersion quality is concerned, can be most sensitively detected by adding various amounts of the flushing aid to a standard pigmented product. If the added amount is significantly incompatible, and added in excess of the tolerance limit, it would cause noticeable pigment flocculation.

Table V shows the compatibility and tolerance limit of three flushing aids in the Centari® product (i.e., 931-0765). The relative amounts of flushing aids with respect to pigment

and binder (solids) are given in columns 2 and 3. The results indicated that when the flushing aids were applied at ~ 7% of the pigment weight, there was no noticeable effect on dispersion quality. Bis(2EH)hydrogen phosphate could be tolerated up to 18% of the pigment weight, while petroleum sulfonate and trioctyl methyl ammonium chloride only to ~ 7%.

(2) Test Method

The above results lay the ground work for a simple test to assess the compatibility level of flushing aids with a given vehicle system. In actual flushing, the amount of flushing aid used ranges from 5%-15% of the pigment weight.

A test procedure can be formulated as follows:

(i) Select a single pigment tint in the product line as a test vehicle - preferably of the same pigment that is to be flushed.

(ii) Add calculated amounts of flushing aid (i.e., 10% or 15% of the pigment weight) to the tint; mix on shaker until uniform (~ 15 minutes).

(iii) Let stand overnight.

(iv) Prepare side-by-side drawdowns against the control.

(v) If no difference can be detected by visual and microscopic (optical) examination, the flushing aid may then be rated as having adequate compatibility for practical application in this product.

A simple test of this kind is needed to screen incompatible flushing aids and reduce the unnecessary further work.

c. Flushing in B-P Mixer

The flushing procedure and practices for presscakes which require the use of flushing aids should be identical to those described in section 3-a.

## 5. Criteria for Selection of Candidate Presscakes for Flushing

### a. Cost Savings Considerations

#### (1) High Toner Content Presscakes

Many dry pigments are not made of 100% toners. Inert additives (such as Blanc Fix, Carbonates, Rosinates, etc.) are blended with the toners to permit the pigment manufacturers to achieve color control and to meet the color specifications. Some of the additives are co-precipitated with the pigments; many more are dry blended. In the latter case, when we buy the presscakes, we buy higher content of toners. For the high cost pigments (i.e., > $10.00/lb.), a 5-10% higher toner content would represent significant savings.

The percent inert additives present in a given dry pigment and its corresponding presscake may not always be available in the trade literature. Such information must be sought from the suppliers for the specific pigments of interest.

#### (2) Presscakes of High Cost Pigments

These are good candidates for "flushing" because an increase of tinting strength, due to finer particle size distribution, would give more dollar value in cost savings.

#### (3) Low-Price Presscakes (relative to the dried counterpart)

A few CPC Blue and Green presscakes (W-765 & W-550) are offered at prices significantly below those of the dry pigments. These should be good candidates for "flushing" and cost savings on their own rights.

If we have an in-house flushing process and technology, the presscake market should be watched closely, so we may use these presscakes to our advantage when they become available.

#### (4) Presscakes of High Volume Pigments

A list of high volume pigments excluding blacks and whites has been put together by A. H. Hamlin. This is attached in the Appendix. This list was compiled on the basis of 1971 Division Consumption. Candidate pigments for flushing (from

the volume list) should also conform with the other criteria of selection.

b. Color Quality Considerations

(1) Particle Size and Size Distribution in Presscakes (i.e., transparent or opaque grade pigments)

The transparent grade pigments, for which the fundamental pigment particles are very small but hard aggregates have been formed during drying, will most likely benefit from "flushing." Examples are W-839, W-819, and W-682, etc.

The converse will be true for the opaque grade pigments.

(2) Mechanical Grindability

As a class, pigments of hard texture and poor mechanical grindability will be good candidates for "flushing."

The mechanical grindability and fundamental pigment size are often closely related (Ref. 12); aggregates of small particles having more area of contact are usually hard to grind.

Soft and easy-to-grind pigments may result from (i) coarse particle size and (ii) resin (or rosinate) treatment (such as co-precipitation, encapsulation, etc.). In our experience, these pigments would offer little incentives for "flushing."

B. Specific Example

The following is a specific example illustrating in full the steps and considerations one probably will have to go through in formulating a flushed dispersion of W-839 for the Centari® refinish enamels.

Referring to the numbers and letter headings of Table I - the Formulation Guidance Chart, each step will be accounted for as follows:

1. Characterization of Presscake

a. Solids

- 30.1% shown on shipping paper by the vendor

- 28.6% average experimental solids based on six random samples

b. Surface Non-Polarity: 75% (see EX-71-33 for method of determination)

This information is not necessary if we choose to use the "Simple Flushability Test" [section (2)].

c. Surface Charge

This information is not needed because W-839 can be flushed without the use of flushing aids.

2. Simple Flushability Test

The test shows the following results:

- The presscake of RT-887-D flushed over directly into the RC-3346 resin phase.
- There was no clear cut water breakout at room temperature. However, the water breakout could be brought about by raising the temperature to 70°C.

This test places the presscake of RT-887-D in the category for which the formulating practices under section (3) of Table I would apply.

3. Presscakes Directly Flushable into Organic Phases

a. Flushing in B-P Mixer

(1) Charging the Mixer

Gallon Weight of W-839 = 12.6 lbs./gallon
Specific Volume ($V_{p.c.}$) of presscake (by Equation I) = 0.108 gal./lb.
B-P mixer working capacity = 2.25 gallon
70% of the working capacity = 1.58 gallon
Presscake (dry basis)/resin ratio in the initial charge = 50/50 = 1

Using equations (1) and (2) (p. 5) to calculate the compositions of initial and 2nd charges, the following flushing procedure is in order:

Flushing Procedure*

| | 1st Portion | 2nd Portion |
|---|---|---|
| RT-887-D presscake | 4900 g. (~ 1400 solids) | 2200 g. (~ 630 solids) |
| RC-3346 | 1400 g. | 630 g. |

(1) Add 1st portion to B-P mixer.

(2) Start unit/bring temperature in steam jacket to ~ 70°C.

(3) Continue mixing until water breakout occurs (~ 30 minutes).

(4) Stop unit.

(5) Decant $H_2O$ [estimate 2700 g. of $H_2O$ to be decanted; use this figure and equations (1) and (2) to calculate the amounts of the 2nd addition].

(6) Add 2nd portion.

(7) Start unit.

(8) Repeat steps 3 through 5.

(9) Add
- RC-3346 750 g. (this brings the resin solids/pigment weight ratio to 45/55 to facilitate the ease of "reduction")
- Toluene 1500 g. (to compensate for the solvent loss to be taking place during vacuum stripping)

(10) Start unit.

(11) Reduce temperature to 50°C/apply vacuum/maintain $N_2$ purge and a vacuum level of 24"-25" Hg/use cold traps (3) to collect condensate and prevent vapor from getting into the vacuum line.

(12) Continue operation for ~ 50 minutes.

(13) Stop unit.

(14) Add toluene 1500 g.

(15) Start unit.

(16) Continue vacuum stripping for ~ 50 minutes.

(17) Check residual $H_2O$ using optical microscope method (see text)/if okay, proceed to the "partial reduction" step.

---

*Experimental Formula Card 40-H-21155, Flushed Violet Centari® Dispersion

Partial Reduction in B-P Mixer

(18) To 17, add a mixture of

| | |
|---|---|
| RC-3346 | 1800 g. |
| Xylene | 1300 g. |

in 20-30 equal portions over a 2-3 hour period.

(19) Empty content of B-P mixer into a pre-mix tank.

(20) Rinse off the material on the wall and the blades with Xylene (~ 1500 g.).

(21) Combine the rinse solution (20) and the flushed dispersion (19).

Final Reduction/"47" Process Sand Grinding

(22) Pre-mix

Reduce the material further in the pre-mix tank with resin/solvent to a viscosity range of 800-1500 cp. A typical formulation could be:

| Entire Content of (21) | |
|---|---|
| RC-3346 | 7800 g. |
| Xylene | 5000 g. |
| Acetone | 500 g. |

(23) Sand mill (30-60 GPH in 8 gallon unit).

(The above flushing procedure was based on an actual run carried out in a 2.25 gallon B-P flusher with a few modifications. This example serves as an illustration; the procedure is not necessarily an optimized one - particularly the "partial reducition operation" which could have been done in a shorter period. The final reduction, as examplified here, would give the flushed dispersion a composition comparable to that of a commercial mill base, 308-839.)

## II. PROCESS SELECTION AND STUDIES

### A. Flushing Equipment

The flushability of a given presscake (i.e., whether it will transfer into the organic phase or remain in the aqueous phase) is governed by the physical and chemical characteristics of the pigment surface. As already illustrated, the non-polar presscakes flush readily into the organic phase; while the polar (or hydrophilic) presscakes require the assistance of flushing aids.

In practice, one must also be concerned with another aspect of "flushing" - namely, the efficiency of flushing as measured by the percentage of the presscake water that can be separated out (and decanted) in a given period of mixing. The efficiency of flushing is closely related to the effectiveness of mixing. Mixing increases the interfacial contact which is a necessary requirement for "flushing" to take place.

We have compared the flushing efficiency of a double arm mixer (Sigma blade Baker-Perkins Mixer) with that of conventional mixing equipment (single shaft propeller mixer). The results are given in Table V. As shown, the B-P mixer is a more efficient flusher than the conventional mixing equipment under various conditions tested. The higher flushing efficiency of the double arm mixer is attributed to its unique design to handle thick and dough-like materials to which class the presscakes belong.

B. Removal of Residual Water

The residual water remaining in the flushed dispersion after decatation is mostly physically trapped. Various methods to remove the residual water have been considered. Some comments of the advantages and disadvantages of each method are given below:

1. Vacuum Stripping

Vacuum stripping is the most commonly used method in the color flushing industry. Water forms azeotropes with a variety of organic liquids which permit distillation of an azeotropic mixture at a temperature significantly lower than the boiling points of the individual components. Coupled with the use of a good vacuum (> 24" Hg), the residual water remaining in the flushed dispersion can be removed effectively within reasonable time (~.5-2.0 hours) at sufficiently low temperatures (50°C-80°C) which will not cause denaturing for most of the organic resins.

Our experiences indicated that effective mixing must be maintained during the vacuum stripping period; otherwise water would be trapped deep inside the highly pasty and dough-like material. Diffusion through this kind of material would be slow if unassisted with mechanical blending.

2. Centrifugation

We have used centrifugation as a method for removing both residual water and coarse particles in one of our flushing processes (ES-71-33). In the last period, we investigated several commercial centrifuges (Sharples Models):

a. A Sharples Super Centrifuge (Model T-1) is suitable for separating immiscible liquids and/or small amounts of coarse particles. The rotor rotates at 15,000 rpm (13,200 X G) and can operate continuously as long as the accumulation of the coarse particles does not exceed the specified limit. For samples in which relatively large amounts of the coarse (e.g., > 20%) particle has to be removed, the unit will have to be stopped frequently for cleaning-up of the accumulated solids.

Besides its usage in connection with our flushing work, we also used the Sharples Super Centrifuge to remove the coarse particles in a commercial two-roll milled dispersion (912-430) and improved drastically the film appearance in terms of clearity and brightness. (Unfortunately, 912-430 was incompatible and flocculated in the Decyl LDL System, and, consequently, the fine quality of this mill base was lost in the letdown stage and never showed up in the final product.) In this regard, we feel that the super centrifugation occupies a unique position in boosting the dispersion quality of existing mill bases and offer new effects in color and styling. The types of mill bases that may best benefit from super centrifugation are those which consist of significant amounts of very fine particles but the overall quality has been averaged down due to the presence of the coarse (most two-roll milled dispersions and some sand milled dispersions of hard-textured pigments may fit into this class).

b. "Westfalia" Centrifuge: The Westfalia Centrifuge has a desludge which automatically (or manually if preferred) discharges the accumulated sludge (coarse solids plus the heavy liquids) and provides truly continuous operation. A laboratory unit (SAMN 205) can process fluid and pumpable liquids up to 60 GPH. This centrifuge is designed to operate at lower rpm (10,000) than the Model T-1 Super Centrifuge.

Some common restrictions to the centrifugation method as a way of clearing out the residual water in the flushing process are:

- The dispersion must be well deflocculated so the fine particles will not be thrown into the discharging stream by the centrifugal force.
- The density of the dispersion must be lower than that of water; this would limit the pigment concentration in the dispersion (e.g., 13-14% if the sp. gr. of the pigment - W-682 - being 3.4)

3. Other Methods

Three-roll and two-roll mills have been described in the literature for removal of residual water following mixer flushing. These methods appear more suitable for 100% solids non-volatile vehicles. With solution vehicles, these methods would give nearly dried products which would then require re-solvation. Process complexity and high operating costs are disadvantages of these methods. Unless justified by unique qualities unattainable otherwise or in special applications, these methods do not appeal favorably as routine processes for removal of residual presscake water.

C. Reduction

The reduction operations to be described in this section apply to flushed dispersions obtained from the Baker-Perkins mixer. At the completion of water removal by vacuum stripping, the mass in the mixer usually was in a highly pasty and semi-plastic state. A partial reduction with solvent/resin would be needed to facilitate emptying it from the B-P mixer.

The partially reduced mixture, however, was still significantly heavier than the average mill base consistency and, sometimes, contained loose unbroken agglomerates. The final reduction is, therefore, (a) to provide a uniform free flowing paint consistency and (b) to break up the loose agglomerates.

Several reduction processes were investigated and their effectiveness compared in the light of the above stated requirements. The results, summarized in the following tabulation, are those of a flushed W-765 dispersion (607-E-42) in a Centari® vehicle (RC-3346):

| | "47" Sand Grinding (Batch) | Cowles Dissolver | "48" Process Mixing | Waring-Blender Mixing |
|---|---|---|---|---|
| Uniformity (macroscopic scale) | Good | Poor; lumps visible to the naked eye | Ok; macroscopically smooth & uniform | Poor; lumps visible to the naked eye |
| Agglomerates (microscopic scale) | Very few; most particles were sub-micron | Poor | Significant number of unbroken agglomerates in the 1-25μ range | Poor |
| Drawdown Film Appearance | Clean; more transparency and less scattering<br><br>(See Figure 1 for optical photomicrographs) | ---- | Slightly hazy; some yellow overtone due to scattering<br><br>(See Figure 1 for optical photomicrographs) | ------ |

These results clearly indicated that among the various processes evaluated, optimum dispersion was obtained through a sand mill procedure.

In addition to the above series of experiments, we also noted that the quality of the flushed dispersion and the ease of "final reduction" varied considerably with the procedure of the "partial reduction" in the B-P mixer (i.e., rate of addition of the reducing resin to the pasty mixture); slow "partial reduction," by dividing up the reducing resin into many small portions (see Sections I-A and I-B) and adding one portion at a time after the previous portion has been completely mixed in, would give rise to a product nearly of the same quality of the sand-mill-reduced dispersion. This is one area in which one should give due consideration in future process optimization. For the present time, however, it appears to me that a "final reduction" with sand milling would iron out the potential variations inherent in the "partial reduction"; eliminate the tedious addition procedure in the "partial reduction" which would otherwise be required; and ensure good (flushed) dispersion quality.

### D. Preferred Flushing Process

Based on the studies and considerations elaborated under the previous subtitles of this section (II), the current preferred flushing process was selected as explained in full in the Formulation Guidance Chart (Table I, section 3). The process consists primarily of (a) flushing and vacuum stripping all residual water in a B-P mixer, (b) partial reduction in B-P mixer, and (c) final reduction with a "47" process sand milling.

The feasibility of super centrifugation with the two Sharples Models (T-1 or SAMN 205) as a way of boosting dispersion quality has been demonstrated. It can be added as a last operation to the current flushing process to give special effect of color and styling if needed.

## III. EVALUATION OF FLUSHED DISPERSIONS

### A. Pigment Range and Scope of Application

A number of organic and inorganic pigments have been investigated in the laboratory regarding their suitability as candidates for flushing. The basis for commercial scale-up must be considered on an individual pigment basis. The criteria

specifically applicable to each pigment are given below (see section I-A-5):

- Higher toner content - W-839, W-819, W-312, etc.
- Presscakes of high cost pigments - W-839, W-819, W-811, Irgazine yellow 2RLT, etc. (> $10.00/lb.)
- Low-price presscakes (relative to dry pigment) - W-765 and W-550
- Presscakes of high volume pigments - W-312 and W-811
- Favorable particle size in presscakes - W-682, W-839, W-819, W-765, and W-764, etc.
- Hard-to-grind pigments - W-839, W-819, W-682, W-844, Irgazine yellow
- Color and styling effect - W-844, (B-5804) (CPC Green with blue overtone)

Among the various pigments which had been preliminarily evaluated, a few were further identified as representative and test pigments for assessment of the feasibility of flushing processes, for costing and in-depth evaluation. These are W-839 (Monastral® Violet R), W-765 (Monastral® Green G), and W-682 (Transoxide Yellow). Flushed dispersions of these pigments will then be evaluated in selected product lines. Our current emphasis is on Centari® refinish enamels because of the anticipated growth of this line of products (ref. 2).

Other product lines and new product areas have been included in this study to demonstrate the scope of application of the flushing technology. A cross section of the various product areas investigated is listed below:

- Centari® refinish enamels (931 line)
- Acrylic refinish lacquers (946 line)
- LDL (980/981 line)
- Dulux® (195 line)
- Powder coating
- Coil coating
- Color concentrate

A summary of the general status, flushing requirements, and results of evaluation is given in Table VI. The comments

and remarks of Table VI should be self-explanatory. The following are some generalized statements abstracted from the results and observations in Table VI.

- The flushed dispersions are formulated to give final compositions similar to those of the existing mill bases.

For the presscakes that require no flushing aids, the ingredients in the flushed dispersions would essentially be the same as those in the commercial mill bases. This practice was instituted to minimize the chances of affecting the properties of the end products. This was borne out by the example of flushed W-839. In so far as has been tested, the flushed W-839 meets the standards (functional properties) of a regular quality control and exceeds the control in tinting strength which is partially expected in view of the higher toner content ($\sim$ 5%) in the presscake. If additional examples to the same effect should be noted, it would provide a basis for lowering our guard against this type of reformulation. The situation could then be handled similarly as that of changing from a sand-mill to a ball-mill procedure for a given mill base formulation.

- While a number of the flushed dispersions (W-839, W-765, W-682, and W-819) showed advantages over the conventional dispersions, others (W-438 presscake and Irgazine yellow presscake) failed to do so. In the latter case, both presscakes contained large hard-to-break crystals. The advantage of "flushing" is very much dependent on the presscake quality. In our experimentation, the crystals in the presscake (or water-wet pigment crystals) have never been found any easier to grind (by conventional sand or ball mills) than the crystals in the dry pigment. Post-flush ball milling of the Irgazine yellow and W-438 presscake yielded products falling significantly short of the transparency quality.

- Comments have been made by independent observers that the films cast from the flushed dispersion (i.e., W-682, W-765, and W-839) appeared cleaner and more saturated in color than those from the conventional dispersions. Provided that these qualities can be preserved throughout the letdown procedures, the cleaner and more saturated color should provide broader latitude for color matching and possibly also better two-tone characteristics. Joint effort with COS will be made to quantify this aspect.

B. High Spot Cost Estimates

The overall cost of a flushed dispersion may conveniently be divided into three components:

(i) Raw Material Cost: Pigment presscakes (on dry basis), in most cases, cost approximately the same as the dry pigments plus a few cents per pound for handling (or shipping). However, a few presscakes (such as W-765, W-550, and W-785), due to competitor's pressure, are being sold at prices 15-25% below those of the dry pigments. In either situation, there will be a differential in raw material costs which should be taken into account.

(ii) Manufacturing Cost: The Baker-Perkins Flusher Process described in earlier sections is basically very similar to the W & P pre-mixing and drying operation - both consist of a mixing (or flushing) step followed by a vacuum drying (or vacuum stripping) step. If we assume that the cost of the Flusher Process is equal to that of the W & P pre-mix/vacuum drying process, a high spot manufacturing cost may evolve from the average Divisional figures (ref. 3) as given below:

| | $/lb. of Pigment Processed |
|---|---|
| "47" Process (overall average) | 0.68 |
| "47" Process - 2 passes | 0.85 |
| W & P Process | 0.95-1.00 |
| Pebble & Ball Mill | 0.95-1.00 |
| Two-Roll Mill | > 2.20 |

Based on these figures, the manufacturing cost of W & P/"47" process will be 10-15¢ (per lb. pigment) higher than that of the 2-pass "47" process.

(iii) Pigment Utility and Tinting Strength: The tinting strength developed from a given amount of pigment is an important factor in cost considerations. Weak tinting strength means poor pigment utility which would be equivalent to a cost penalty; while strong tinting strength represents high pigment utility and provides a cost credit.

1. In-House Flushed Dispersions vs. Purchased Dispersions

To provide a picture of the costs of in-house flushed dispersion vs. purchased ones, two examples will be cited.

The first example is a flushed phthalo green. The composition of a flushed commercial phthalo green and a quotation of it were obtained from Hilton-Davis through the Raw Material Group. The cost of an in-house flushed dispersion of the same composition was then computed and compared with the quoted price. The results are summarized as follows:

| | In-House Flushed Dispersion | Hilton-Davis' Quotation |
|---|---|---|
| Total cost/lb. of dispersion[1] | 0.84[2] | 1.185 |
| Cost/lb. of dry pigment consumption | 4.66[2] | 6.58 |

The second example involves an inorganic pigment, transoxide yellow (W-682). We have flushed this pigment into RC-3346 resin for the Centari® refinish enamels. Currently, the color of transparent yellow in the Centari® line products is relying on a purchased dispersion W-642 from Inmont. Preliminary evaluation by M. H. King of Flint R & D Laboratory showed that the enamel product formulated from the in-house flushed W-682 dispersion was superior to that based on W-642 in color quality and two-tone characteristics (see Table VI). Should the in-house flushed dispersion be able to replace W-642 in the Centari® line in the future, the comparative costs would be as follows:

| | In-House Flushed Dispersion | Hilton-Davis' Quotation |
|---|---|---|
| Total cost/lb. of dispersion[3] | 0.534[2] | 1.62 |
| Cost/lb. of dry pigment consumption | 2.67 | 8.10 |

[1] Composition of dispersion - CPC Green/alkyd resin solids/solvent - 18/34/48

[2] See letter I. C. Chu to T. A. Ashe for detailed calculation (6/22/72)

[3] Composition - Transparent yellow iron oxide/Cooks resin/solvent - 20/13.3/66.7

The preceding examples show that the total costs of in-house flushed dispersions are considerably lower than the prices paid for the purchased dispersions. The mark-up of phthalo green dispersion (by Hilton-Davis) is ~ 40% and that of W-642 (by Inmont) is ~ 200%. The savings on each pound of phthalo green pigment used would be $1.90 and the savings on each pound of yellow iron oxide consumed would be $5.40.

2. Flushed Dispersions vs. 2-Pass "47" Process Dispersions

The comparative costs of flushed dispersions and 2'pass "47" process dispersions will be illustrated with the following examples.

The first example will be the flushed CPC green (W-765) dispersion vs. an equivalent "47" process dispersion (assuming the tinting strength is equal):

| | Flushed Dispersion | 308-765 |
|---|---|---|
| Cost/lb. of dispersion[1] (10.5% of pigment) | 0.589[2] | 0.694 |
| Cost/lb. of dry pigment consumption | 5.61 | 6.61 |

The second example will be the flushed Monastral® Violet R (W-839) vs. an equivalent "47" process dispersion (i.e., 308-839):

| | Flushed Dispersion | 308-839 |
|---|---|---|
| Cost/lb. of dispersion[3] | 1.121[2] | 1.203 |
| Cost/lb. of dry pigment consumption | 12.43 | 13.37 |

[1]Composition - W-765/RC-3346/solvent - 10.5/45/44.5

[2]See letter I. C. Chu to T. A. Ashe for detailed calculation (6/22/72

[3]Composition - W-839/RC-3346/solvent - 9/55/36

In the case of the CPC green (W-765), there is a cost differential of ~ $1.00 per pound of pigment in favor of the flushed dispersion. This is due primarily to the difference in raw material cost. We have not yet determined the tinting strength credit, if any. The calculation is therefore based on equal tinting strength between the flushed and "47" process dispersions.

In the case of the Monastral® Violet R (W-839), there is also a cost differential of ~ 94¢ in favor of the flushed dispersion. Here the savings is due primarily to the tinting strength credit (see Table VI).

3. Summary

To sum up, the high spot cost studies illustrated above indicate that:

- In-house flushed dispersions would be considerably cheaper than equivalent dispersions purchased from outside dispersion houses. In the two given examples, the savings range from ~ $1.90-$5.40 per pound of dry pigment.
- The major cost item in a dispersion formulation is the pigment cost. Manufacturing cost by "47" and flushing processes contribute 10-20% to the total cost for pigments priced over $3.00/lb. For the iron oxide pigments (~ $1.20/lb.), the manufacturing cost accounts for 30-40% of the total dispersion cost.

  Consequently, for a relatively high cost pigment, increase of tinting strength or a lower presscake price would be sufficient to balance slight manufacturing cost penalty and contribute to lowering the overall dispersion cost.
- The cost differential between flushed dispersions and 2-pass "47" process dispersions is in the range of $1.00/lb. of pigment subject to basic presscake pigment prices and tinting strength variation.
- Other potential quality advantages such as cleaner and more saturated color are difficult to attach a dollar value. They are not being considered in this cost study but should be set aside as a separate item.

- Flushed dispersion quality approaching ball mill or two-roll quality would represent added cost advantages on a relative basis since the latter are more costly processes than the 2-pass "47" process as shown by average Divisional figures.

REFERENCES

1. I. C. Chu, EX-71-33

2. Letter A. H. Hamlin to I. C. Chu, 11/4/72

3. Letter J. L. Evans to I. C. Chu, 5/15/72

4. Letters J. G. King to I. C. Chu, 12/7/71 and 5/12/72

5. M. H. King - personal communication

6. Letter F. Rohrbacher to I. C. Chu, 6/8/72

7. L. R. Harper - personal communication

8. Mike Miller - personal communication

9. J. R. Moffett - personal communication

10. R. D. Anderson - personal communication

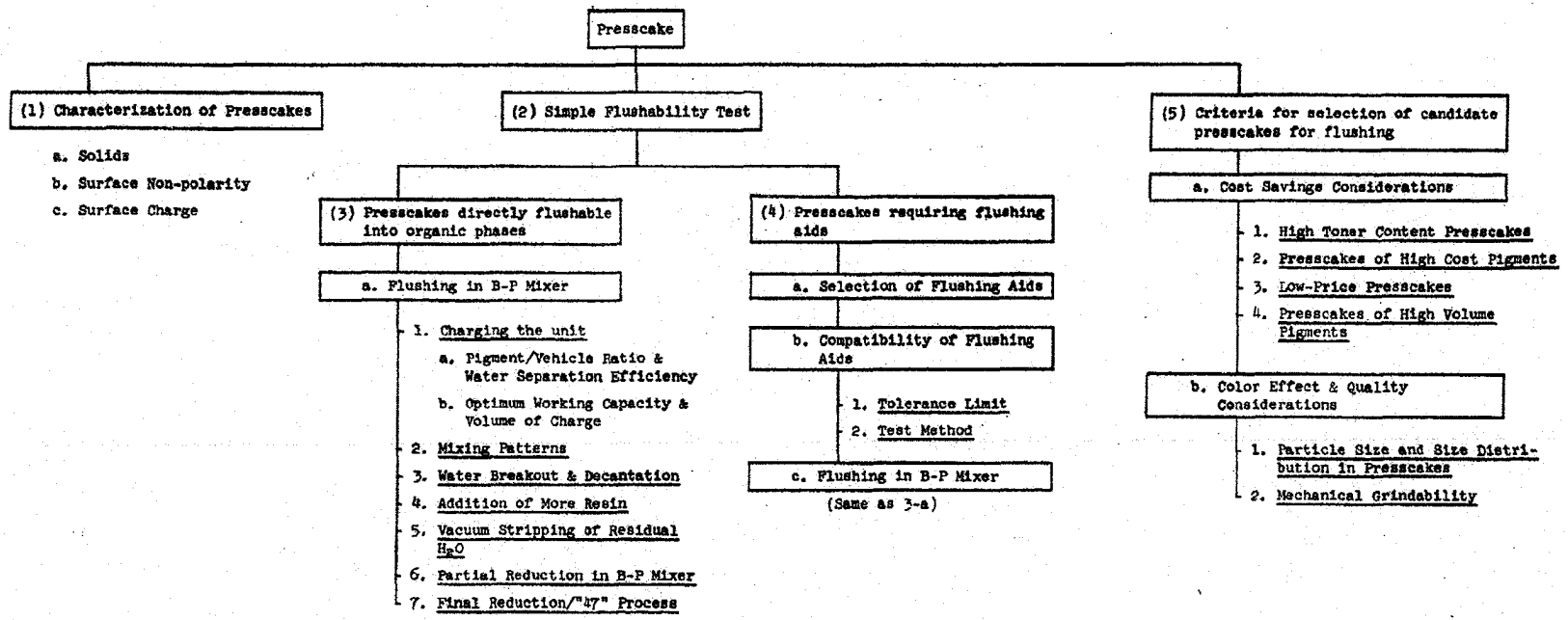
11. L. R. Andrews - personal communication

12. C. Manger (Pigments Department) - personal communication

ICC/ayk
6/28/72

TABLE I

FORMULATION GUIDANCE CHART FOR FLUSHED DISPERSIONS




ICC/ayk
6/14/72

TABLE II

EFFECT OF PRESSCAKE/VEHICLE RATIO ON EFFICIENCY OF $H_2O$ SEPARATION**

| GT-792-P* Presscake / RC-3346 (Presscake (dry basis)/ vehicle - wt. ratio) | Decantable $H_2O$ (g)* | Remarks |
|---|---|---|
| 460/150 (57/43) | 198 | Mixture very stiff & tough |
| 460/200 (50/50) | 194 | Good mixing consistency |
| 460/250 (44.5/55.5) | 141 | |
| 460/300 (40/60) | 79 | |

*GT-792-P is equivalent to W-765

**Evaluation was carried out in a quart size B-P mixer at room temperature; duration of mixing = 10 minutes.

ICC/ayk
6/14/72

TABLE IIa

EFFECT OF PRESSCAKE/ORGANIC SOLVENT RATIO ON $H_2O$ SEPARATION EFFICIENCY

| GT-792-P* Presscake / Toluene | Presscake (dry basis)/ Solvent - wt. ratio | Decantable $H_2O$ (g) |
|---|---|---|
| 460/100 | 66.6/33.4 | 204 |
| 460/150 | 57/43 | 202 |
| 460/200 | 50/50 | 200 |
| 460/250 | 44.5/55.5 | 164 |
| 460/300 | 40/60 | 130 |

*GT-792-P is equivalent to W-765.

ICC/ayk
6/14/72

TABLE III

FLUSHING AGENTS FOR TRANSOXIDE YELLOW PRESSCAKE (W-682)[1]

| Flushing Agent | Type | Rating of Flushing Efficiency[2] |
|---|---|---|
| Capric acid ($C_{10}$) | Anionic | 5 |
| Bis(2EH)hydrogen phosphate | Anionic | 5 |
| Isooctyl acid phosphate | Anionic | 5 |
| Phenyl acid phosphate | Anionic | 5 |
| Octyl phenyl acid phosphate | Anionic | 5 |
| Stearic acid ($C_{18}$) | Anionic | 4 |
| Behenic acid ($C_{22}$) | Anionic | 4 |
| Triethanolamine myristate | Anionic | 4 |
| Sodium petroleum sulfonate (MW 340-500) | Anionic | 4 |
| Sodium caprate and stearate | Anionic | 1 |

[1]W-682 has a positive surface charge of $\sim$ +44 MV at pH $\cong$ 6.8

[2]Flushing efficiency was rated by the residual coloration of the aqueous phase 1 $\longrightarrow$ 5; No flushing $\longrightarrow$ complete transfer

ICC/ayk
6/28/72

TABLE IV

COMPATIBILITY AND TOLERANCE LIMIT OF VARIOUS FLUSHING AIDS IN CENTARI® VEHICLE*

| Flushing Aid | Pigment/Flushing Aid (Wt. Ratio) | Binder/Flushing Aid (Wt. Ratio) | Effect on Pigment Dispersion |
|---|---|---|---|
| Bis(2EH)Hydrogen Phosphate | 1.0/0 | 100/0 | Slightly Def. |
| | 1.0/0.073 | 100/0.53 | " " |
| | 1.0/0.18 | 100/1.30 | " " |
| | 1.0/0.54 | 100/3.80 | Flocculated |
| | 1.0/0.90 | 100/6.50 | " |
| | 1.0/1.25 | 100/9.00 | Severely Floc. |
| Petroleum Sulfonate (Alconate 80) | 1.0/0.073 | 100/0.53 | Slightly Def. |
| | 1.0/0.18 | 100/1.30 | Flocculated |
| | 1.0/0.54 | 100/3.80 | " |
| | 1.0/0.90 | 100/6.50 | " |
| Trioctyl Methyl Ammonium Chloride (Aliquat 336) | 1.0/0.073 | 100/0.53 | Slightly Def. |
| | 1.0/0.18 | 100/1.30 | Flocculated |
| | 1.0/0.54 | 100/3.80 | Severely Floc. |
| | 1.0/0.90 | 100/6.50 | " " |

*Test was made by adding indicated amount of flushing aids to a single pigment mixing machine product (931-0765); let the mixture stand overnight; evaluate microscopically the dispersion quality.

ICC/ayk
6/14/72

TABLE V

$H_2O$ DECANTATION EFFICIENCY

(Double Arm Mixer vs. Single Shaft Propeller Mixer)

| Presscake (dry basis)/ Organic phase (wt. ratio) | % Presscake $H_2O$ Decantable* Baker-Perkins Mixer (Qt. size) | Single Shaft Propeller Mixer |
|---|---|---|
| (A) GT-792-P/Toluene: | | |
| 40/60 | 50% | 28% |
| 45/55 | 63% | 36% |
| 50/50 | 77% | 51% |
| 57/43 | 77% | 52% |
| 67/33 | 78% | 48% |
| (B) GT-792-P/RC-3346: | | |
| 40/60 | 31% | 13% |
| 45/55 | 54% | 45% |
| 50/50 | 75% | 70% |
| 57/43 | 76% | -- |
| 67/33 | -- | -- |

*GT-792-P Monastral® Green Presscake had an average solids of 43.6%; total presscake $H_2O$ was calculated on this basis. Percent decantable $H_2O$ was determined after 10 minutes of mixing.

ICC/ayk
6/28/72

## TABLE VI

### FLUSHED DISPERSIONS & SCOPE OF APPLICATION

| Notebook Reference | W-Code | Pigment Name | Dispersion Line | Product Line | General Comments and Preliminary Evaluation | Evaluation by Product Group | Flushing Process & Additional Remarks |
|---|---|---|---|---|---|---|---|
| 607E-42 | W-765 | Monastral® Green G | 308 | Centari® Refinish Enamels (931 line) | a) Can be flushed into RC-3346 without the use of flushing aids<br>b) Presscake priced at ~ $1.15 below dry pigment cost ($3.15/430)<br>c) Flushed dispersion showed greener and cleaner color | Flushed sample has been submitted to Flint for evaluation | a) Baker-Perkins Flusher Process |
| 567E-146 | W-839 | Monastral® Violet | 308 | " " | a) Can be flushed into RC-3346 without the use of flushing aids<br>b) Flushed dispersion showed 6.2% stronger tinting strength (by wet cell method) and > 10% stronger based on drawdowns<br>c) 931-Line single pigment tinting quality showed the flushed dispersion to be much cleaner and free of grit | a)*[1] Color, viscosity, and settling stability were good for at least two month stored at room temperature, 140°F, or under mixing machine conditions<br>b)*[1] Gloss, hardness, & gasoline resistance were equal to control<br>c)*[1] Tinting strength was significantly greater than a regular quality control<br>d)*[1] COS reported that the flushed dispersion was shadable to meet color specifications for 931-0839<br>e)*[1] Solvent composition was essentially Rule 66 conforming | a) 567E-146 was prepared by a "Kettle" flushing/vac. dist./"47" process ("Kettle" Flushing Process)<br>b) It was demonstrated that flushing could also be carried out in Baker-Perkins mixer<br>c)*[1] References for Evaluation Results are attached in Appendix II |
| 567E-198 | W-642 | Transoxide Yellow | 308 | Centari® Refinish Enamels (931 line) | a) Flushing aid - Bis(2EH)hydrogen phosphate was used at ~ 8% level based on pigment weight<br>b) Drawdown film appeared very transparent and clean | a)*[2] Metallic sprayouts showed better two tone characteristics than those drived from purchased yellow dispersion (W-642)<br>b)*[2] Yellower and cleaner (without the undesired red overtone) color was noted with the flushed dispersion | a) 567E-198 was prepared - "Kettle" flushing followed by centrifugation |
| 607E-23 | W-642 | " " | 308 | " " | Same as above | Flushed sample has been submitted to Flint for evaluation | a) Baker-Perkins Flusher Process |
| 567E-190 | W-438 Press-cake | Hydrous iron oxide (Harmon color) | 308 | " " | a) Flushing aid - Bis(2EH)hydrogen phosphate was used<br>b) Drawdown film appeared somewhat hazy<br>c) Presscake contained > 50% coarse which impaired quality | a)*[2] Drawdown film quality was judged unsatisfactory | a) "Kettle" flushing followed by Ball Mill |
| 567E-99 | W-811 | Monastral® Red Y | 308 | " " | Preliminary evaluation showed no advantages over a regular quality control (i.e., 308-811) | --- | a) "Kettle" Flushing Process |
| 567E-134 | W-819 | Monastral® Red B | 913 | Acrylic Refinish (946 line) | a) Can be flushed into RC-3176 without the use of flushing aids<br>b) Tinting strength was significantly higher than a regular quality control | --- | a) "Kettle" Flushing Process |
| 567E-111 | -- | Irgazine Yellow 2RLT | 913 & 308 | 946 line & Centari® (931 line) | Irgazine yellow 3 RLT (W-673) and 2RLT presscakes contained large crystals; sand & ball milling could not break up these crystals effectively<br>Flushed dispersions, even after ball milling, failed to show film clearity and transparency | --- | a) "Kettle" Flushing Process |
| 567E-151 (and -41) | W-682 | Transoxide Yellow | 912 | LDL (980/981 line) | a) Flushed with Bis(2EH)hydrogen phosphate (8% on pigment weight)<br>b) Stabilized with RC-M-5581 in toluene<br>c) Drawdown films appeared transparent and free of grit | a)*[3] The flushed dispersion equaled 2-roll quality in the old LDL system (RC-5401)<br>b)*[3] The flushed dispersion was flocculated in the Decyl LDL/RL-3340 system; consequently the metallic panels were poor in transparency and two-tone characteristics | a) "48" process mixer flushing/ centrifugation |

*[1] Evaluated by J. L. Evans, Flint R & D Laboratory

*[2] Evaluated by M. H. King, Flint R & D Laboratory

*[3] Evaluated by J. G. King, Flint R & D Laboratory

ICC/eyk
6/23/72

TABLE VI (Continued)

FLUSHED DISPERSIONS & SCOPE OF APPLICATION

| Notebook Reference | W-Code | Pigment Name | Dispersion Line | Product Line | General Comments and Preliminary Evaluation | Evaluation by Product Group | Flushing Process & Additional Remarks |
|---|---|---|---|---|---|---|---|
| 567E-148 | W-312 | Thiofast Red | 42 | Dulux® (195 line) | a) Can be flushed into RC-305 without the use of flushing aids<br>b) Flushed dispersion appeared smooth and intense in color - we have not made any quantitative evaluation | | a) "Kettle" Flushing Process |
| 607E-14 | W-764 | Monastral® Green Y | -- | Powder coating | a) Can be flushed into plasticizer RC-G-35118 without the use of flushing aids<br>b) Microscopic examination showed finer particle size distribution in 607E-14 than a regular 901-764 quality | a)*4 Panels prepared from the flushed dispersion (607E-14) exhibited significantly higher gloss (ca. 10-12 units) and better image definition (1-2 units) than those from the 901-764 quality | a) Baker-Perkins Flusher Process |
| 567E-81 | W-811 | Monastral® Red Y | -- | Powder coating | a) Same as above | a)*5 Panels prepared from the flushed dispersion (567E-80) exhibited better flow and higher film gloss than those prepared from dry W-811 pigment | a) Simple stirrer flushing |
| 567E-9 | B-C-1-p | α - phase CPC blue | -- | Color Concentrate | a) Can be flushed into A-B dispersant (544E-103) without the use of flushing aids | To be evaluated by E. J. Zinser | a) Baker-Perkins Flusher Process |
| 567E-83 | PVF dispersion | | -- | Coil Coating | a) Flushed with Bis(2EH)hydrogen phosphate into propylene carbonate | a)*6 Flushed PVF dispersion gave good film, free of grits and agglomerates<br>b) Flushed PVF has been formulated into coil coating enamels in 8 colors; pigmented films exhibited good coalescence, high gloss, and toughness<br>c) Panels prepared from flushed PVF enamels are now undergoing exposure tests | a) Single stirrer flushing |

*4 Evaluated by F. Rohrbacher, Experimental Station Laboratory

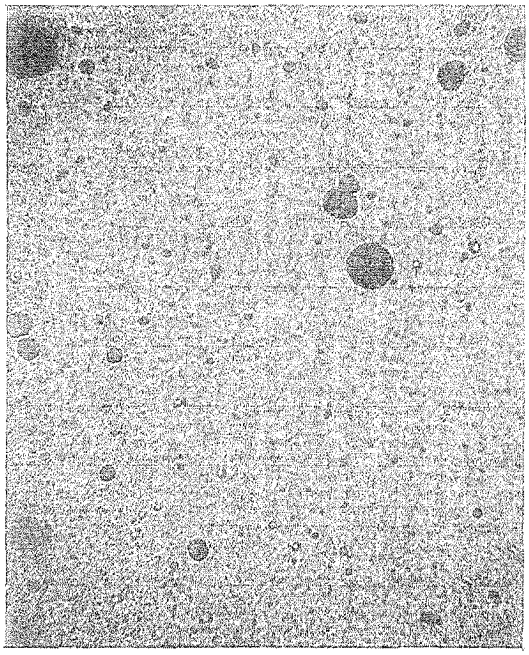
*5 Evaluated by L. R. Harper, Experimental Station Laboratory

*6 Evaluated by Mike Miller, Marshall Laboratory

ICC/ayk
6/26/72

FIGURE 1

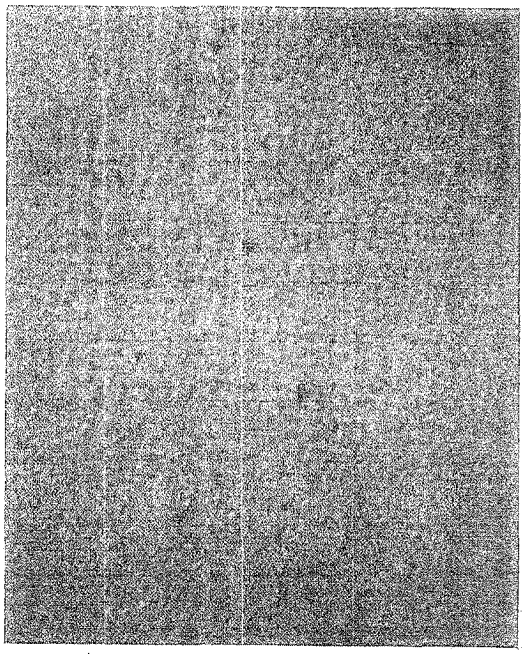
OPTICAL PHOTOMICROGRAPHS OF FLUSHED DISPERSION BY VARIOUS REDUCTION PROCESSES



Flushed W-765 Dispersion
(607E-42)
Reduced by "48" Process

Scale: 240X

Estimated particle
size: 1-25 microns
(Excluding the fine
background)



Flushed W-765 Dispersion
(607E-42)
Reduced by Sand Milling

Scale: 240X

Estimated particle
size: $\leq$ 1 micron
(Excluding the fine
background)

ICC/ayk
6/28/72

cc: D. J. Troy, ESL
T. A. Ashe, ESL

APPENDIX I
Page 1

Not Indexed
File: 212579

Experimental Station
November 1, 1971

I. C. CHU
F & F DEPARTMENT
EXPERIMENTAL STATION

PIGMENTS FOR CONSIDERATION FOR FLUSHING*

I have reviewed the consumption of pigments and purchased dispersions for the 6-months period ending April, 1971. It should be noted that this period covers most of the GM strike and, therefore, may be somewhat lower than normal. The attached list shows the ones with annualized usage of over $25,000 excluding fillers (china clay, barytes, etc.), aluminum paste, whites and blacks. It includes 62 items which amount to approximately $9MM of annualized purchases. Based on this, any small reduction in usage would be reflected as a substantial increase in profits to the Department.

A. H. Hamlin

A. H. HAMLIN

AHH/bap

Attachment

*Updated list shown in Appendix IV

## PIGMENT CONSUMPTION

(Over $25,000/yr. cal.)

| Name | W Code | Yr. to Date | Six Months 11-70 4-71 | Cost Cal. 6 Months | Price/lb. |
|---|---|---|---|---|---|
| Bon Red Dark | 300 | 20,337 | 26,121 | 59,541 | 2.28 |
| Thio Fast Red | 312 | 8,949 | 14,837 | 78,979 | 5.32 |
| Hi-Ox Red Lead 97% | 349 | 75,117 | (12) 117,414 | 22,105 | .19 |
| Precip Iron Oxide | 362 | 82,907 | (11) 128,858 | 23,285 | .18 |
| Precip Iron Oxide | 392 | 139,606 | (5) 229,700 | 41,578 | .18 |
| Mon. Maroon Rt 792D | 393 | 3,040 | 4,132 | 50,996 | 12.34 |
| Red Shade Transp DI | 400 | 5,329 | 28,507 | 45,658 | 1.60 |
| Midas Gold RL 3244 | 424 | 51,486 | (13) 100,602 | 61,194 | .61 |
| #19 Brown | 437 | 16,581 | 23,073 | 20,584 | .89 |
| Flush Hydr Iron Ox | 438 | 17,958 | 38,097 | 47,127 | 1.24 |
| Ferric Hydnate Disp | 454 | 35,131 | 48,086 | 43,713 | .91 |
| Midas Gold Disp | 460 | 71,643 | (14) 93,602 | 242,899 (3) | 2.60 |
| Monastral Blue | 505 | 17,170 | 28,755 | 97,220 | 3.38 |
| Monastral Blue | 530 | 7,042 | 11,498 | 13,064 | 1.14 |
| Mon. Blue Bt 383D | 550 | 1,503 | 3,758 | 12,749 | 3.39 |
| Mon. Blue BL 282D | 551 | 6,440 | 8,111 | 21,119 | 2.60 |
| Monastral Blue GE | 552 | 2,444 | 3,335 | 12,260 | 3.68 |
| Phthalocyanine B. L. | 557 | 16,003 | 19,541 | 58,441 | 2.99 |
| Indo Fast Violet | 559 | 993 | 1,383 | 22,642 | 16.37 |
| Phthalocyanine Blue | 560 | 4,574 | 5,774 | 28,528 | 4.94 |
| Milori Blue | 582 | 28,017 | 51,502 | 32,433 | .63 |
| Indo Fast Violet LA | 589 | 2,114 | 2,712 | 12,035 | 4.44 |
| Sun Yellow N | 608 | 35,495 | (18) 56,259 | 54,811 | .97 |
| C. P. Zinc Yellow | 609 | 305,240 | (3) 450,885 | 164,101 (5) | .36 |
| Green Gold YT562D | 612 | 12,464 | 18,886 | 115,639 (10) | 6.12 |
| | | | First Sub-Total | 1,382,701 | |

## PIGMENT CONSUMPTION

(Over $25,000/yr. cal.)

| Name | W Code | Yr. to Date | Six Months 11-70 4-71 | $ Cost Cal. 6 Months | Price/lb. |
|---|---|---|---|---|---|
| Molybdate Orange | 622 | 93,078 | (10) 139,279 | 82,514 | .59 |
| Dalomar Yellow YW-731P | 628 | 11,768 | 16,125 | 15,786 | .98 |
| Ferr Yellow Orange | 630 | 348,351 | (2) 545,613 | 85,674 | .16 |
| Yellow Shade Transparent | 642 | 8,132 | 11,988 | 19,219 | 1.60 |
| Red Tone Mol Orange | 652 | 35,676 | 50,136 | 29,916 | .60 |
| YT-714-D Green Gold | 653 | 5,624 | (17) 60,672 | 41,511 | 6.22 |
| Red Red Toned Moly | 655 | 128,138 | (6) 192,415 | 113,344 | .59 |
| Orange Toner | 658 | 5,483 | 8,075 | 128,764 (9) | 15.95 |
| Krolor Orange | 665 | 13,608 | 17,414 | 21,679 | 1.25 |
| Indofast Yellow | 672 | 2,606 | 3,256 | 70,931 | 21.79 |
| Irgazin Yellow 3RLT (?) | 673 | 39,348 | (20) 54,491 | 653,490 (1) | 11.99 |
| Irgazin Yellow | 678 | 1,538 | 1,812 | 21,770 | 12.01 |
| C.P. Chrome Yellow | 679 | 38,053 | (16) 66,929 | 29,312 | .44 |
| Chrome Yellow Med. | 686 | 474,719 | (1) 729,724 | 314,097 (2) | .43 |
| Chrome Yellow X2777 | 687 | 105,205 | (7) 155,916 | 65,270 | .42 |
| Krolor Yellow Med. | 690 | 8,250 | 12,250 | 11,944 | .98 |
| Monastral Gold | 691 | 862 | 1,638 | 20,128 | 12.29 |
| Titanium Yellow | 694 | 13,807 | 19,188 | 17,196 | .90 |
| Mon. Green GI-761D | 750 | 6,466 | 9,616 | 32,923 | 3.42 |
| Chrome Oxide LT | 754 | 35,913 | (15) 77,941 | 39,376 | .51 |
| Phthalo Green Yellow | 764 | 8,720 | 11,816 | 56,269 | 4.76 |
| Monastral Green | 765 | 8,915 | 11,730 | 45,560 | 3.88 |
| Mon. Green GT-674D | 785 | 22,761 | 36,265 | 140,555 (6) | 3.88 |
| Dark Tol Red Disp | 800 | 34,360 | (19) 56,008 | 48,461 | .87 |
| Thio Fast Red Luke | 804 | 15,770 | 18,810 | 60,012 | 3.19 |
| Scarlet Toner RG-500 | 807 | 1,072 | 1,457 | 22,432 | 15.40 |
| Monastral Red | 811 | 8,589 | 11,672 | 127,669 (8) | 10.94 |
| Monastral Maroon B | 816 | 1,200 | 3,108 | 38,197 | 12.29 |
| Monastral Violet | 818 | 7,445 | 12,429 | 136,260 (7) | 10.96 |
| | | | Second Sub-Total | 2,489,159 | |

## PIGMENT CONSUMPTION

(Over $25,000/yr. cal.)

| Name | W Code | Yr. to Date | Six Months 11-70 4-71 | $ Cost Cal. 6 Months | Price/lb. |
|---|---|---|---|---|---|
| Mon. Red B RT-706D | 819 | 1,183 | 2,803 | 30,637 | 10.93 |
| Mon. Violet RT-887D | 839 | 2,883 | 4,852 | 51,887 | 10.69 |
| Monastral Maroon | 842 | 13,285 | 18,420 | 226,247 (4) | 12.28 |
| Perrindo Maroon | 856 | 5,886 | 8,716 | 110,233 | 12.65 |
| Light Tol Red Disp | 862 | 90,270 | (9) 139,499 | 106,771 | .77 |
| Toluidine Toner Lt. | 865 | 5,397 | 7,461 | 13,379 | 1.79 |
| Iron Oxide | 870 | 172,707 | (4) 252,891 | 21,531 | .09 |
| Red Iron Oxide | 878 | 113,651 | (8) 144,357 | 12,670 | .09 |
| | | | Total | 573,355 | |
| | | | First Sub-Total | 1,382,701 | |
| | | | Second Sub-Total | 2,489,159 | |
| | | | GRAND TOTAL | 4,445,215 | |





10/27/71

FF-5521 REV. 6-70

APPENDIX II

cc: L. W. Crissey, Flint
L. I. Miller, Flint

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED
FLINT, MICHIGAN 48502

PLEASE REFER TO OUR FILE:

FABRICS AND FINISHES DEPARTMENT
FLINT RESEARCH AND DEVELOPMENT LABORATORY

May 11, 1972

I. C. CHU Esp Station
~~F&F~~
WILMINGTON

W-839 DISPERSION FOR "CENTARI", 567-E-146

We are currently evaluating flushed "Monastral" Violet (W-839) dispersion coded 567-E-146. Our evaluation is not yet complete but at this time the following observations can be made concerning a single pigment tinting enamel based on 567-E-146:

1. Color, viscosity and settling stability are good for at least one month when stored at room temperature, 140°F. or under Mixing Machine conditions. Stability results will be completed in about two months.

2. Gloss, hardness and gasoline resistance are equal to a regular quality control.

3. Tinting strength is significantly greater than a regular quality control in one test.

4. COS reported that a Laboratory sample of the tinting was shadeable to meet color specifications for 931-0839.

Our evaluation does not include any long term durability testing. Wet stability tests will be terminated at three months.

FLINT R & D LABORATORY

J. L. Evans
J. L. Evans

JLE/bw

cc: J. B. Lyman, ML
J. J. Sanderson, ML
P. E. Wills, ML
C. N. Swinehart, Flint
A. F. Nugent, Flint
R. Moses, Ch. Wks, Orchem
D. M. Marsh, ESL
H. L. Jakubauskas, ESL

Not Indexed
File: 211104

Experimental Station
April 5, 1972

**APPENDIX III**
**Page 1**

TO: T. A. ASHE
F & F DEPARTMENT
EXPERIMENTAL STATION

FROM: I. C. CHU, F & F, ESL

## ORGANIC TITANATE (TLF 2005)*

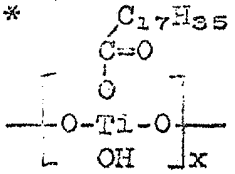
Organic Titanate TLF 2005 used as a surface treatment agent for pigments has been reported** to give encouraging results in a 864-line white.

Samples of TLF 2005 in aqueous emulsion and solid forms were obtained from R. Moses of Orchem and evaluated as a pigment dispersing aid in various aspects. Our findings are summarized as follows:

- TLF 2005 as a Dispersion Stabilizing (or Deflocculating) Agent

  A pigment dispersion of W-819 (15% pigment) in toluene was prepared by sand grinding (Red Devil Shaker) using TLF 2005 as stabilizing agent (15-20% TLF 2005 based on pigment weight). The dispersion exhibited a fair degree of fluidity but the pigment particles were flocculated. An equivalent dispersion prepared with A-B dispersant (RCH-5581) exhibited high degree of fluidity and well deflocculated pigment. These results indicate that TLF 2005 is a mediocre dispersant. While effective for the easy-to-stabilize pigments (i.e., $TiO_2$ and inorganic pigments), it is inadequate for the organic pigments.

---

* 

**Staff note, February, 1972

o TLF 2005 as an Aid for Pigment Grindability

TLF 2005-treated and untreated transoxide yellow (W-682) samples were ball milled in a Centari© vehicle (RC-3346). We noted no significant difference in color and transparency development as a function of the milling time between the treated and untreated samples.

o TLF 2005 as a "Flushing" Aid

Attempt was made to flush the presscake of transoxide yellow pigment (W-682) from the aqueous into the organic phase using the aqueous emulsion of TLF 2005 as flushing agent. TLF 2005 was found not effective at all in this respect.

R. Moses has been advised of the above results and comments in telephone conversations. I suggested that an Organic Titanate with a pendant carboxyl group in place of the hydroxyl group could be a more effective pigment dispersant, and Organic Titanates with ionic characteristics may promote specific adsorption (in aqueous phase) on pigment surfaces to a greater extent than the non-ionic types. R. Moses will make effort to prepare the Organic Titanates of the suggested types and provide them for F & F's evaluation when they are available.

ICC/ayk
4/5/72

## APPENDIX IV

### CANDIDATE PIGMENTS FOR FLUSHING*

[Selected on basis of (1) volume, (2) unit price, (3) grindability, and (4) glamour quality]

| W Code | Pigment Name | Consumption Six Months (11/71→4/72) | | |
|---|---|---|---|---|
| | | lb. | $ | Unit Price |
| 300 | Bon Red Dark | 30,840 | 74,442 | 2.41 |
| 312 | Thiofast Red | 12,415 | 79,356 | 6.39 |
| 393 | Mon. Maroon RT-792-D | 4,338 | 53,168 | 12.26 |
| 505 | Monastral Blue | 30,190 | 110,813 | 3.67 |
| 537 | Monastral Blue | 3,894 | 14,170 | 3.64 |
| 550 | Mon. Blue BT-383-D | 3,324 | 12,363 | 3.72 |
| 551 | Mon. Blue BL-282-D | 10,588 | 30,155 | 2.85 |
| 552 | Mon. Blue BT-417-D | 3,346 | 12,249 | 3.66 |
| 557 | Phthalocyanine B. L. | 17,113 | 55,661 | 3.25 |
| 558 | Mon. Blue RF BT-427-D | 1,384 | 5,086 | 3.68 |
| 559 | Indofast Violet | 1,472 | 25,874 | 17.58 |
| 560 | Phthalocyanine Blue | 7,532 | 39,246 | 5.21 |
| 576 | CPC | 2,693 | 7,404 | 2.75 |
| 577 | Mon. Blue BT-413-D | 370 | 1,347 | 3.64 |
| 588 | Ind. Bluf BP-242-D | 2,323 | 56,340 | 24.25 |
| 608 | Sun Yellow N | 49,195 | 47,488 | 0.97 |
| 612 | Green Gold YT-562-D | 22,281 | 136,043 | 6.11 |
| 653 | YT-714-D Green Gold | 5,067 | 30,941 | 6.11 |
| 658 | Orange Toner | 5,406 | 88,802 | 16.43 |
| 663 | Midas Gold Yellow | 8,694 | 23,934 | 2.75 |
| 664 | Indofast Yellow | 417 | 7,060 | 16.93 |
| 665 | Krolor Orange | 59,333 | 77,390 | 1.30 |
| 672 | Indofast Yellow | 760 | 16,941 | 22.23 |
| 682 | Transoxide Yellow | 16,347 | 18,831 | 1.15 |
| 691 | Monastral Gold YT-793-D | 1,000 | 12,311 | 12.31 |
| 752 | Phthalo GRE Ex. Yellow | 1,252 | 4,782 | 3.82 |
| 764 | Phthalo Green Yellow | 27,517 | 130,112 | 4.72 |
| 765 | Monastral Green A-751-D | 7,583 | 32,238 | 4.25 |
| 785 | Mon. Green GT-674-D | 33,070 | 143,021 | 4.33 |
| 804 | Thiofast Red Lake | 19,524 | 64,468 | 3.46 |
| 807 | Scarlet Toner RG-500 | 1,434 | 23,296 | 16.25 |
| 811 | Monastral Red RT-759-D | 17,013 | 185,864 | 10.93 |
| 816 | Mon. Maroon B RT-849-D | 2,996 | 36,776 | 12.28 |
| 818 | Mon. Violet RT-795-D | 13,434 | 146,618 | 10.91 |
| 819 | Mon. Red B RT-796-D | 4,784 | 52,287 | 10.93 |
| 820 | Newport Maroon RT-647-D | 301 | 3,295 | 10.95 |

*Updated list, June, 1972

CANDIDATE PIGMENTS FOR FLUSHING* (Continued)

| W Code | Pigment Name | Consumption Six Months (11/71→4/72) | | |
|---|---|---|---|---|
| | | lb. | $ | Unit Price |
| 839 | Mon. Violet RT-887-D | 10,454 | 109,746 | 10.05 |
| 842 | Mon. Maroon RT-920-D | 1,291 | 15,820 | 12.23 |
| 844 | Mon. Magenta RT-203-D | 1,084 | 14,373 | 13.26 |
| 851 | Mon. Red B RT-742-D | 100 | 1,090 | 10.95 |

*Updated list, June, 1972

ICC/ayk
7/19/72

ABSTRACT

A "Preferred Flushing Process" using a heavy duty Baker-Perkins Mixer was described. A "formulation guidance chart" which gave step-by-step processing and formulating instructions was included.

Flushed dispersions were formulated from a range of presscakes and their scope of application in various finishes products illustrated. High spot comparative costs of flushed vs. purchased and "47" process dispersions were developed.

The role of "flushing" as an alternative way to manufacturing pigment dispersion was assessed and a course of action recommended.

## DISTRIBUTION LIST

| Copy No. | Full Reports |
|---|---|
| 1 | J. C. Richards, Wilm. |
| 2 | G. I. Mulholland, Wilm. |
| 3 | J. E. Griffiths, Legal, Wilm. |
| 4 | R. E. Fay, Wilm. |
| 5 | R. W. Laurrell, Marshall Lab |
| 6 | E. A. Andre, Marshall Lab |
| 7 | J. B. Lyman, Marshall Lab |
| 8-10 | Library, Marshall Lab (3) |
| 11 | F. M. Gavin, Flint |
| 12 | L. W. Crissey, Flint |
| 13-14 | Central Report Index, Secy's, Centre Road (2) |
| 15 | P. L. Mitchell, Parlin |
| 16 | N. G. Fisher, CRD, ESL |
| 17 | D. M. Marsh, ESL |
| 18 | W. M. Duffy, ESL |
| 19-21 | File Room, ESL (3) |
| 22 | T. A. Ashe, ML |
| 23 | R. E. Funer, ESL |
| 24 | I. C. Chu, ESL |

First Parts

W. D. Lawson, Wilm.
J. A. Klacsmann, Wilm. ) In turn
N. Pappas, Wilm. )
S. R. Miller, Wilm. )
R. S. Prengle, Wilm. ) In turn
K. F. Browning, Wilm. )
A. J. Wells, Wilm.
C. W. Stahl, Wilm.
T. R. Matthews, Wilm.
E. T. Breuer, Wilm.
R. E. Pike, Wilm.
E. K. Holden, Wilm.
J. K. Leahy, Wilm.
C. N. Swinehart, Flint
P. M. Hodgson, Flint
A. W. Andresen, Marshall Lab
C. E. De Boer, Marshall Lab
W. Waldron, Marshall Lab
H. S. Wellman, Marshall Lab
S. Hochberg, Marshall Lab
W. S. Zimmt, Marshall Lab
G. E. Lewis, Marshall Lab
D. M. Glenn, Marshall Lab
C. H. Knop, Marshall Lab (16)
R. H. Vining, Phila. Plt.
A. V. Scancella, Fairfield
ESL Supervisors, Associates, and Fellows (12)