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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT
PROGRESS REPORT

HF MILLING OF PHTHALOCYANINE PIGMENTS - I
STUDIES IN ACETONE

Period Covered: JUNE, 1949 - DECEMBER, 1950.

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NEWARK PLANT

PIGMENT COLOR RESEARCH REPORT

PROGRESS REPORT

TITLE: HF MILLING OF PHTHALOCYANINE PIGMENTS - I
STUDIES IN ACETONE

PERIOD COVERED: JUNE 1949 - DEC. 1950

CHARGE: A-II-C-261

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APPROVED BY: J. R. Cooper 8/21/52 DATE ISSUED: AUGUST 22/52.

INTRODUCTION

In the summer of 1949, confidential information was received from the Fabrics and Finishes Department that a new method of dispersing pigments in liquids had been developed, and it was suggested that the method might have application in the Pigments Department, particularly in the particle size reduction of phthalocyanine pigments.

Two visits were made to the Philadelphia Laboratories of F & F and full information was supplied to the Pigments Department, including sketches and actual inspection of plant equipment and the privilege of reading several reports. Equipment similar to their laboratory equipment was set up at Newark and an extensive program of research has resulted. The objectives have been to effect more efficient particle size reduction of phthalocyanine pigments and/or to do it at a lower cost than is possible in the present ball mill operation.

When this work was undertaken, it was considered highly confidential and the terminology, "HF Milling", was adopted to distinguish it from any F & F terminology. The issuance of U.S. Patent 2,581,414 (Hochberg to DuPont) has removed any further reason for special secrecy.

This report will be largely confined to operations using acetone as the liquid medium. A subsequent report in the series will cover operations wherein water is the liquid in which the pigment is dispersed.

SUMMARY OF RESULTS

A process, considerably modified from that originally given to us, has been developed for grinding Phthalocyanine Blue LB and Polychloro phthalocyanine Green in acetone in the laboratory in a cycle of about 1 hour and with a power consumption in the order of 1-1.5 horsepower hour per pound of pigment, which is about 1/3 to 1/2 the power consumption of the Newport ball mills. Particle size reduction was also obtained with Blue BG, but a much longer time was required for change to the desired beta phase and this process was not worked out in detail. The process was applied in a limited manner with fair success to certain vat dyes under consideration as pigments.

Semi-works studies were also conducted on Blue LB with similar success, as well as limited studies on CPC Green.

In spite of the successful reduction to practice in the semi-works, cost studies did not show a marked saving over the ball mill process, and it was not possible to justify replacing the ball mills already in operation. The process offered some quality advantages, but did not eliminate the hazard inherent in the operations with acetone; rather, this hazard would probably be greater, due to a somewhat greater difficulty in preventing the escape of vapors from the mill.

The possibility of continuous operation was explored very briefly and is believed to be quite promising, subject to the hazards inherent in the operations with acetone.

PATENT STATUS

U.S. 2,581,414 (Hockberg to DuPont) covers the original F & F process. However, the claims are quite restricted and are limited to a process using Ottawa Testing sand. Hence, they do not cover the process as contemplated at Newark. No other patents are known which will restrict our use of the process.

It is believed that there are patentable aspects of the process, both as described in this report and when water is used as the liquid as will be described in a subsequent report. The following art is known to be pertinent to this process.

Loukomsky (U.S. 2,486,304) obtains beta phase CPC by subjecting the alpha phase pigment to intensive mixing and shearing attrition in the form of a shearable magma of pigment and crystallizing liquid. Although dough mixers are specifically disclosed, the claims are not so limited. It might be difficult to write a broad claim around this patent.

U.S. 2,574,597 and the similar B'nt. Pat. 654,795 (both Celanese patents) disclose the preparation of a water dispersible dye by milling a paste of the dye with water, a lignin sulfonate and a neutral or alkaline water soluble salt. The claims also include a means of directly drying as by spray drying. There is no limitation as to the type of milling.

It is planned to file one or more applications of the process and it is hoped that a basis can be found for novelty in the product when ground with water.

DESCRIPTION OF PROCESS AND EQUIPMENT

Essentially the HF process involves the application of an intensive shearing action to a suspension in a liquid of a mixture of the pigment and a finely divided inert solid. The inert solid is separated from the pigment suspension and the pigment isolated by conventional means.

The equipment used has been similar to that adopted by F & F. The shearing action has been obtained by essentially smooth discs approaching the diameter of the vessel and operating at fairly high speeds. In the laboratory, a drill press has served as the source of power, driving a shaft on which is mounted two smooth stainless steel discs 1/4" thick by 4" diam. and 1-1/2" apart. They operate in a stainless steel beaker about 5" in diameter mounted with a full length cooling jacket. Speeds up to 2450 RPM have been used. A similar setup was designed for the semi-works using a larger drill press, a jacketed 13 gal. container of 14" diameter and two 9" discs at about 900 RPM. This was operated successfully, but a more convenient setup was arranged using the same container, but applying power through a single 10" disc driven by a Cowles Dissolver at considerably higher speeds. A larger container, 22 gals. and 19" diameter, has been used with fair success. The attached sketches show this equipment in more detail.

In the original development by F & F both batch and continuous operations were contemplated, but all plant development used a continuous process in which the coarse sand employed as the inert solid was retained in the grinding vessel by a fine screen (80-100 mesh), through which the pigment dispersion passed freely. Retention time was controlled by the rate of withdrawal from a reservoir surrounding the screen. Since sand did not prove to be a satisfactory inert solid for this work and since screening was not an acceptable method of removing the solids used for the pigment suspension, the work at Newark has all been conducted as a batch operation.

In general the desired charge of pigment, liquid and inert solid has been added to the grinding unit, agitation contained for an arbitrarily chosen time and the whole charge transferred to another vessel in which the mixture was diluted with the grinding liquid, or with water, until the inert solid would settle more rapidly than the finely ground pigment which was removed by decantation. Since the preferred inert solids were water soluble salts, final separation was effected by solution of the solid in a normal extraction procedure. Acetone removal and final extractions were done in the manner already developed for acetone milling.

DISCUSSION OF THE EXPERIMENTAL RESULTS

In a process such as this, there are a great many variables which require study and many of them are interdependent. Some of them are purely mechanical, such as the arrangement of the equipment, the speed of agitation and the like. The nature of the inert solid, the proportion of pigment to inert solid, the viscosity of the mixture, the use of dispersing agents and many others of a like nature also required consideration. All of these will be discussed below in an attempted logical sequence, not necessarily related to the order in which the work was done.

The first experiment was done in June, 1949 in the Philadelphia Laboratory, when Messrs. Horning and Hochberg of F & F and Stratton of the Pigments Department agitated a mixture of CPC LB crude, acetone and Ottawa sand in a 1 qt. can with 2 glass discs for about 1 hour. The entire mixture was brought to Newark, the pigment separated from the sand by dilution and decantation and extracted by the normal procedure (dilute acid followed by ammonia wash). The resulting product had a strength approximately mid-way between that of the original crude and standard acetone ground CPC BT-284-D. This result was considered encouraging, and equipment was obtained and arranged for further work at Newark.

In almost the first experiment a pair of glass discs obtained from F & F were cracked. They were considered too hazardous for regular use and were placed with 1/4" stainless steel discs. These were eroded quite badly with sand. Also, with sand, grinding proceeded rather slowly after an initial rapid pick up in strength.

Finally, the complete removal of sand proved very difficult, if not impossible, and the problem of residual grit loomed very large. At this juncture, Dr. F. F. Ehrich suggested that a crystalline water soluble salt, such as sodium chloride (NaCl), be tried in place of sand, since the ordinary extraction procedures would remove it without trouble. This proved to have a marked advantage over sand in strength of product after a given grinding cycle, and it eliminated completely both the residual grit and the erosion of the plates. Trial of other crystalline salts indicated that the size of the crystal had more influence than the nature of the salt in most cases. Thus NH_4Cl, Na_2SO_4 $(NH_4)_3$ PO_4 and the like gave more rapid grinding than NaCl. Eventually, pulverized NaCl became the solid of choice because of availability and low cost, coupled with excellent performance. Subsequently, powdered borax ($Na_2B_4O_7 10H_2O$) was shown to be equally good and the solubility change with temperature offered interesting possibilities of recovery which have never been thoroughly explored in the case of acetone grinding. As a subsequent report on aqueous grinding will show, borax became the agent of choice with water as the liquid. A few inorganic salts, notably calcium carbonate and sodium carbonate seemed to give markedly inferior results. One attempt to use barytes as the inert solid resulted in the surprising observation that separation of pigment and barytes could not be effected under any conditions of dilution. Furthermore, there was little evidence of strength development. On the other hand a very fine sea sand gave results approaching those from the powdered inorganic salts. Very fine steel shot also showed fair performance as to particle size reduction, but the separation and prevention of corrosion appeared very unattractive.

The mechanical conditions within the grinding unit proved to be important, as would be expected, but no critical optimum was discovered in any case. Rather, these seemed to be important only as they influenced the efficiency of power usage. In general, particle size reduction has proved to be almost a direct function of power consumed, regardless of the equipment. In the 5 inch container, discs of 3, 3-1/2 and 4 inches diameter were used with the advantage always in favor of the largest discs. Varying the distance between the discs and the distance from the bottom of the container had only a minor influence on pigment strength. The speed of rotation influenced the rate of particle size reduction very much, but the power consumption per pound of pigment finished remained about the same. Thus, higher speeds gave more rapid grinding at a higher power consumption in terms of time. Much of the work in the lab unit was done at 2450 RPM.

The total charge in the unit and ratio of pigment to inert solid have been varied widely but a clear cut optimum has not been established. The larger pigment charges grind more slowly but, again, the power consumption per unit of color is a major factor. Nevertheless, there appears to be some point at which the rate per

unit of color suffers. This point was not clearly established and may vary with the design of the unit. In a similar manner, the ratio of color to solid was varied, and there seems to be a rather indefinite point at which the increased time required more than offsets the increased charge possible. The optimum weight ratio varies with the specific gravity of the solid, but the volume ratio has appeared to be fairly constant in the range of 10 to 12 volumes of inert solid (wt/sp gravity) per volume of pigment. The volume of liquid has always been kept at the minimum required to insure good flow of the charge under the influence of the agitator. Some work on thinner slurries seemed unfavorable. The laboratory charge was finally fairly well standardized at 55-60 gm pigment, 1000 gm pulverized NaCl (or 800 gm powdered borax) and about 500 cc acetone. The semi-works charges were close volume scale-ups of the laboratory charges.

Various dispersing agents were added to determine their effect in the milling operation. No such agent showed any significant or consistent improvement in the rate of grind in acetone. Among the agents tried, may be mentioned sodium benzoate, Triton X-100, Turkey Red Oil and Antarox A-200.

In considering the recovery and re-use of the inert solid grinding aid, it was quickly shown that neither gravity nor centrifugal settling would effect separation at the grinding consistency. Dilution by a factor of 3 to 5 was necessary to bring about such separation. To use this much acetone was undesirable to say the least. On the other hand, to dilute with water to this extent meant the loss of most of the NaCl by solution. With borax, on the other hand, it was possible to recover 60% or more by decantation or by solution, filtration and recrystallization. However, the use of recovered borax without drying would introduce a significant amount of water into the system, so a study of the use of dilute acetone of various concentrations was therefore undertaken. The presence of water in such grinds tended always to reduce the efficiency of the milling, but in the range from 100% acetone to about 50% acetone the loss in efficiency was small. Below 50% acetone, the efficiency dropped off very markedly, so that unsatisfactory results were the rule. This work, however, led to attempts at grinding crude press cakes. The first such attempt was a semi-works grind of an unusually low kerosene (2-3%) semi-works press cake, and it resulted in an unexpectedly high strength and rapid grind. However, subsequent work with the dry counterpart of this crude indicated superiority over the press cake. Furthermore, the grinding of press cakes with normal kerosene contents (20-30%) was uniformly unsuccessful, and even dry crudes with high kerosene gave poor results in 100% acetone. Apparently dilute acetone can be used only with quite pure crudes. The behavior of many grinds, particularly those with kerosene present, in dilute acetone was very odd, giving the appearance that the pigment had extracted the organic liquid from the mixture and separated as a pasty mass from the water borax slurry. After this occurred, there was little, if any, further grinding and the peculiar appearance remained through extraction and drying.

A torque table was arranged for one of the laboratory units and power consumption measurements were made on this device. As expected, the actual power usage varied with the speed of agitation, but a surprising amount of power was applied to the 2 qt. can in the lab unit. For instance, at 2450 RPM the power required was approximately 0.2 HP. The power consumption per pound of color includes the factor of time of grinding which also varied with the speed. In these grinds, the rate leveled off after an initial rapid gain, much as it does in a ball mill. However, the time required to approximate standard strength in laboratory grinds was less than 2 hours at 1250 RPM and less than 1 hour at 2450 RPM. In one series, for instance, 2 hours at 1250 RPM was very close in results to 1 hour at 2450 RPM giving a very dark MF about 10% strong and intense vs BT-304-D. The power consumption per lb. of pigment finished at this level in this series was 1.2-1.5 HP. hrs., which compares with over 3 HP. hr. per lb. in the Newport mills.

In view of the F & F experience, supported by some work on this process by Orchem, continuous grinding by the HF process was considered a distinct possibility. Although no attempts have been made to retain the inorganic salt in the unit with the pigment slurry passing through a screen, attempts to screen out the solid as a separate operation have been unsuccessful in the absence of substantial dilution. Continuous operation, therefore, is considered possible only through continuous feeding of all ingredients and withdrawal of the whole grinding mass for subsequent processing elsewhere. Such a process has not actually been tried, but was simulated by withdrawal of an aliquot sample and replacement with unground crude blue, borax and acetone at fairly short intervals after an initial standard cycle. There was no significant deterioration in quality of such samples over a succession of cycles and it seems reasonable to conclude that a continuous operation of this type would be successful. Later work on aqueous grinding also supports the belief that a continuous separation of the borax could be worked out. In short, a completely continuous operation seems to be technically possible, though the economic soundness is questionable.

A few isolated experiments of a miscellaneous nature deserve mention. One attempt to use a draft tube, such as now used on many processes in the Newark plant, to obtain the desired intensive shear gave evidence that it was much less effective than the HF unit. No measure of the efficiency in power usage was made, but the operation lacked many of the attractive features of the HF unit and was not pursued further. It has been suggested, but not tried, that the Abbe Lenart mixer be used in this work.

One experiment using glycerine as the grinding liquid on the theory that high viscosity would promote particle size reduction was not successful.

It was suggested that CPC pigment should grind itself

instead of requiring a grinding aid in the form of an inert salt. A sample ground for 7 hours showed no change in strength after the first few minutes and the maximum change was only of the magnitude to be expected from an additional extraction.

Attempts to use a "Syntron" Vibrator to remove the salt or borax from the ground slurry were unsuccessful. Large particles of solid, such as sand, can be removed from a liquid with this device, but very small particles do not migrate beyond the pool of liquid.

One attempt to use the HF mill as a salt milling device for "Dispersion Milling" (salt and a solvent) was partially successful in that there was a considerable strength increase and some evidence of partial phase change. However, complete fluidisation of the mass was not obtained and there was serious dusting, so it was not an attractive operation.

APPLICATION TO CHLORINE-FREE BLUE

Since the only chlorine-free crude CPC readily available when this work was done, was a sulfated type comprising a mixture of alpha and beta phases in an indefinite proportion, some phase change was required to obtain a typical Blue BG product. HF grinding with chlorine-free Blue gave normal strength development, but it required several hours (at least 5-6 hours) to obtain any significant phase change; and products of the desired greenness were never obtained. The addition of Perclene to the grinds seriously reduced the strength obtainable. Grinds in kerosene were also quite weak. It is probable that HF grinds of the "EF" type crude now available in acetone would give a beta form product of desirable properties.

POLYCHLORO CPC GREEN

The work on green was quite limited, but appeared to follow the principles elaborated above. Attempts to grind a Newport crude of known poor quality were no more successful than in a ball mill. Some grinds were successfully made without an oxidising agent present, but there is insufficient experience to justify any conclusion on this.

MISCELLANEOUS GRINDS

Two vat dye pigments were ground in the HF mill with results which largely conform to the above principles and to the behavior of these same colors in other solvent milling procedures.

"Ponsol" Red RL is a red oxadiazole vat dye which has given variable hue in different methods of finishing. HF grinding in acetone gave a bluer, duller hue than other methods and did not show much promise.

"Lithosol" Violet 4 RN is a vat dye formerly used with

CPC in "Pocono" Blue BP-243-D. It was ground successfully in the HF unit and serious consideration was given to a plant installation for this purpose. However, the potential sales did not seem to justify the installation and work on this color was dropped.

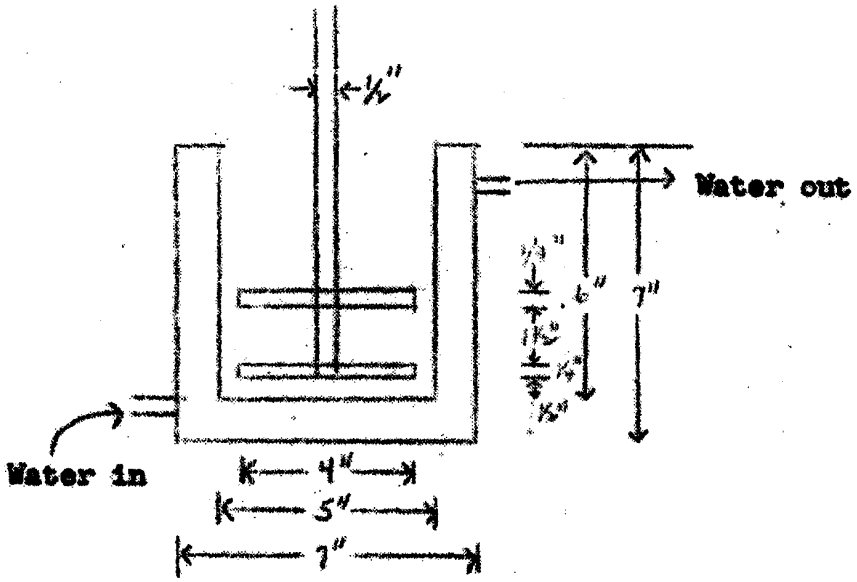
SEMI-WORKS STUDIES

The following table summarizes the data from grinds made in the semi-works.

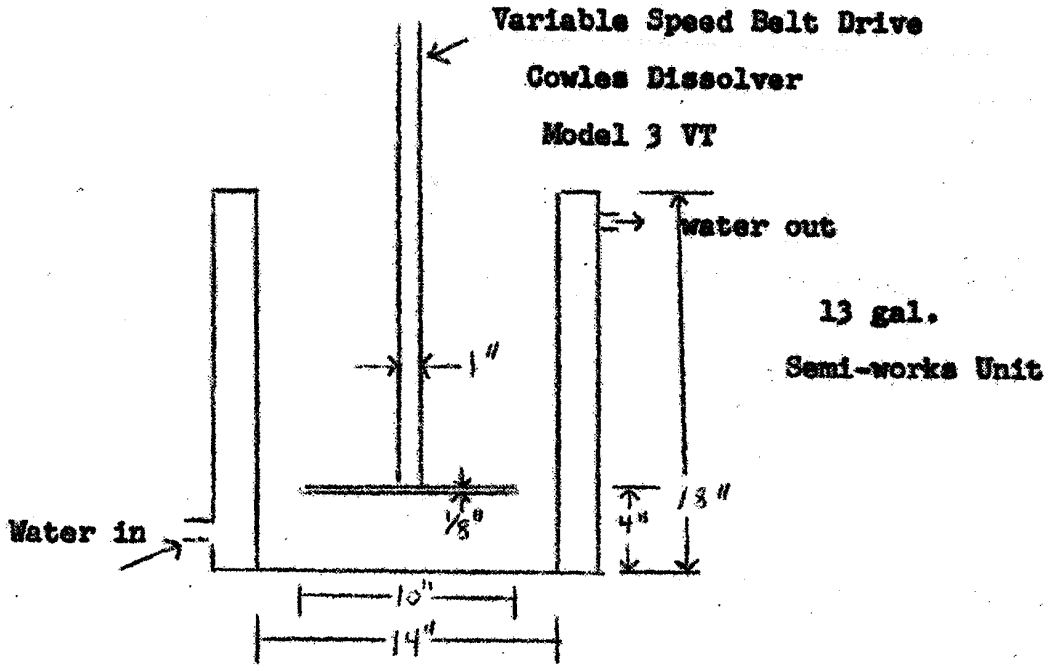
EXPERIMENTAL DETAILS

The work summarized in this report is recorded in the following notebooks:

NB 1190
NB 1191
NB 1345
NB 1383



LABORATORY UNIT



13 gal.

Semi-works Unit

RECORD OF SEMI CHARGES

Lot #	Equipment	Speed	Disc. Diam.	Pigment	Lbs. Pigm.	Salt	Lbs. Salt	Liquid	Agent Used	Time	Time to Std. St.	Final Sts.	Notes
2136	Drill press	600	2-9"	Lot 329	3	NaCl	57	acetone	--	4 hrs.	3 hrs.	97	
2137	" "	600	"	"	3.5	"	66	"	--	4	3-1/2	98	
2230	" "	600	"	"	3.5	borax	51	50% "	Triton X-700	4-1/2	--	weak	separation
2231	" "	600	"	"	"	"	51	" "	--	4	--	"	"
2284	" "	700	"	"	"	"	51	" "	--	4	2-1/2	98	
2315	New Drill Press	715	"	"	"	"	51	acetone	--	3	1-1/2	90-93	
2335	Cowles	690	6"	"	"	"	51	"	--	3	--	weak	
2348	"	1150	8"	"	"	"	51	"	--	3	1-1/2	93-95	
2349	"	1500	8"	"	"	"	51	"	--	3	1	90-93	
2354	"	1725	6"	"	"	"	51	"	--	3	1-1/2	95	
2355	"	2160	4"	"	"	"	51	"	--	3	--	weak	
2362	"	1500	8"	2361 PC	"	"	51	" slightly dilute	Antarox A-200	3	1/2	90-93	
2379	"	"	8"	2361 dry	"	"	51	acetone	"	3	1	90-93	
2385	Cowles 25gal.	"	8"	Lot 329	"	"	51	"	--	3	2	97	
2386	" "	"	8"	"	7	"	102	"	--	3	3	100	
2399	Cowles 13gal.	"	8"	Lot 454PC	3.5	"	51	"	Antarox A-200	3	--	weak	24.5% Kerosene
2400	" "	"	8"	455-PC	3.5	"	51	"	"	3	--	weak	26.0% "
2401	" "	"	8"	456 PC	3.5	"	51	"	"	3	--	"	32.3% "
2402	" "	"	8"	457 PC	3.5	"	51	"	"	3	--	"	29% "
2403	" "	"	8"	454 dry	3.5	"	51	"	"	3	1/2	95	9.7% "
2404	"	"	8"	455 dry	3.5	"	51	"	"	3	1	100	13.8 "
2405	" "	"	8"	456 dry	3.5	"	51	"	"	3	1-1/2	100	19.7 "
2406	" "	"	8"	457 dry	3.5	"	51	"	"	3	1/2	97	8.8 "
2407	" "	"	8"	Lot 329	4.5	"	38	"	--	3	2-1/2	99	--
2408	" "	"	8"	"	7	"	35	"	--	3	--	104	
2410	" "	"	8"	2361 PC	3.5	"	51	"	--	3	1	90-93	
2420	" "	"	8"	454 baked	3.5	"	51	"	Antarox A-200	3	1	95	0.62% "
2421	" "	"	8"	455 baked	3.5	"	51	"	"	3	1	95	0.51% "
2422	" "	"	8"	456 "	3.5	"	51	"	"	3	1	95	0.31% "
2423	" "	"	8"	457 "	3.5	"	54	"	"	3	1	95	0.55% "

Lot #	Equipment	Speed	Disc. Diam.	Pigment	Lbs. Pigm.	Salt	Lbs. Salt	Liquid	Agent Used	Time	Time to Std. St.	Final Sts.	Notes
2438	Cowles 13gal.	1500	8"	OU 6087	3.5	borax	51	acetone	--	3	1	97	9.9% Kerosene
2439	" "	"	"	"	3.5	"	"	"	antarox A-200	3	1	97	" "
2454	" "	"	"	826 PC	3.5	"	"	"	--	3	--	weak	31.1% "
2455	"	"	"	" "	3.5	"	"	"	antarox A-200	3	--	"	" "
2442	" "	"	"	267 Cl free BG	3.5	NaCl	"	kerosene	--	5	--	weak	
2460	" "	"											
2460	" "	"	"	BGPC	3.5	borax	"	acetone	--	8	3	(at 3 hrs. weak (& dull at 6 hrs.	
2461	" "	"	"	steam dist PC	3.5	"	"	"	--	8	2	100	beta phase
2389	Cowles 13gal.	1500	8"	Orchem PC MDD-1888	5.2	borax	75	acetone	chrom-ate	3	2	95	
2483	" "	"	"	Nwpt. PC Lot 182	3.5	"	51	"	no "	3	1	95	blue
2484	" "	"	"	" "	3.5	"	51	"	chrom-ate	3	1-1/2	95	blue
2353	" "	"	"	Violet 4 RN	3.5	borax	51	acetone	--	3	2-1/2	100	vs lab control
2375	" "	"	"	" "	3.5	NaCl	66	"	--	3	1/2	98	" " "