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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

BT-449-D - QUALITY IMPROVEMENT

Period Covered March, 1967 - January, 1968

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PIGMENT COLOR RESEARCH REPORT

SUBJECT: BT-449-D - QUALITY IMPROVEMENT

Period Covered: March, 1967 - January, 1968

SUBMITTED BY: E. E. JAFFE E.E. Jaffe Date Submitted 12/1/68

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TABLE OF CONTENTS

		Page
I.	HISTORICAL INTRODUCTION	1
II.	CONCLUSIONS	1
III.	ACKNOWLEDGEMENT	2
IV.	DISCUSSION	2
	1. Mechanism of Breaching	2
	2. Desirable Properties of Breaching Solvents	5
	3. Emulsion Stability Considerations	6
	4. Breaching with CCl_4	8
	5. Dispersibility of Plant CCl_4-Breached Products	8
	6. Migration in Vinyl and Hydrolysis of CCl_4	9
	7. Perclene as Breaching Solvent	11
	8. Perclene - Emcol P-10-59 Combination	13
	9. Plant Breaching with Perclene	14

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I. HISTORICAL INTRODUCTION

BT-449-D, a breached semichloro copper phthalocyanine (CPC) specifically designed for easy dispersibility in vinyl was introduced to the trade by DuPont in 1962. The pigment found fairly wide acceptance for pigmentation of plastics and some application in inks.

The preparation of this pigment entailed breaching of premilled CPC containing 3.8 to 4.5% chlorine with ortho-dichlorobenzene (ODCB) followed by batch distillation of the organic solvent, acid extraction, pressing, laking with 5% calcium Staybelite, drying and pulverization. All processing steps up to the laking procedure were carried out at Newport and the remaining steps at Newark

Unfortunately, since the introduction of this code, there has been a nearly continuous quality problem of borderline or inferior vinyl dispersibility as determined by minimum dispersive effort, such as five cuts in vinyl on a two roller mill. Strength by rubout has similarly been variable and frequently outside shipping limits.

Several processing difficulties were recognized by J. H. Braun and subsequently F. L. Reig. (1) The chlorine content in the pre-milled crude was frequently outside the designated limits. (2) After apparently complete distillation of the breaching solvent, the product contained substantial amounts of ODCB. To eliminate the latter difficulty, studies were initiated to (a) use a flash distillation unit for complete solvent removal and shorter and more controlled contact time between the ODCB and pigment, and (b) use other less potent and lower boiling solvents in the breaching operation.

A study by D. H. Eastham* led to the installation of a flash distillation unit at Newport. The demonstration that carbon tetrachloride (CCl_4) can serve as a breaching solvent (patent proposal J.H.Braun #1603-K) led F.L.Reig to work out a process using a specific surfactant (G-3300) which gave good results in laboratory experiments. Although the introduction of the CCl_4 process in conjunction with the flash distillation unit into the plant had a beneficial effect on pigment dispersibility, in general, plant-produced pigment continued to be dull and reproducibility in dispersibility was not good. In addition, a serious corrosion problem was encountered in the Newport plant.

II. CONCLUSIONS

It has been demonstrated in the laboratory, Semi-Works, and the plant that BT-449-D of good quality, requiring no extenders, can be produced by extensive modifications of the old process. The changes involve the substitution of perchloroethylene (Perclene) for ODCB as the growth solvent, improved emulsification of the organic solvent in the pigment slurry, change from batch to flash distillation for removal of the organic solvent, and an improved extraction procedure for the removal of base-soluble impurities and a substantial part of the emulsifying agent used to promote emulsification.

*Report KN-67-15

A problem related to the tendency of the pigment to bleed under certain filtration conditions from alkaline medium remains to be resolved at Newport. Progress has been made toward the resolution of this problem.

III. ACKNOWLEDGEMENT

Close and effective cooperation during the plant phases of this investigation from F.L.Reig (Newport)and R.F.White (Newark) is gratefully acknowledged.

IV. DISCUSSION

The approach to the solution of the problem has been to determine the basic parameters in the breaching operation and subsequent processing steps which are responsible for variations in dispersibility and strength of BT-449-D.

1. Mechanism of Breaching

One of the first requirements in this study was to find a physical method for rapid and reasonably accurate determination of the primary particle size in a breached pigment, either directly or by a proportional parameter. In addition, an accurate determination of the amount of β-CPC present in a breached product was desirable.

To determine the amount of β-CPC in a breached product with some degree of accuracy, a series of mixtures of α-free β-CPC (BT-297-D, lot 00994) and β-free α-CPC (BT-304-D, lot 00704) were prepared (1869/3). The mixtures contained 2.5, 5, 7.5, 10, 15, and 20% β-CPC. A plot of the 9.2 to 6.6 2θ peak height ratio vs. % β phase content as determined from patterns obtained at 1°/min. was linear at low % β content but curved off at higher percentages of β phase. A straight line was obtained over the entire range of concentrations when the peak height ratio was plotted against the ratio of % β over % α-CPC. A similar plot was obtained from patterns run at the regular speed of 2°/min. This method is reliable provided the measured α- and β-phases possess the habit exhibited by the standards used in the preparation of the reference plot.

In an attempt to determine primary particle size, the easily measured $\beta_{1/2}$ (half width of a prominent peak in the X-ray diffraction pattern) could not be applied in this case since the prominent peak in the X-ray pattern is a doublet and, in addition, most products contain variable amounts of β-CPC making the determination of $\beta_{1/2}$ on most peaks an unreliable measurement of the particle size. Fortunately, the use of the so-called valley parameter* due to the valley between the peaks at 26.6 and 27.5 2θ values is not interfered with by the presence of small and variable amounts of β-CPC. The valley parameter (v.p.) can be defined by the expression $\frac{AB}{AC} \times 100$ based on the drawing in Fig. 1, where $AC = \frac{a + b}{2}$.

*C.W.Manger, Report KN-68-4, p.10

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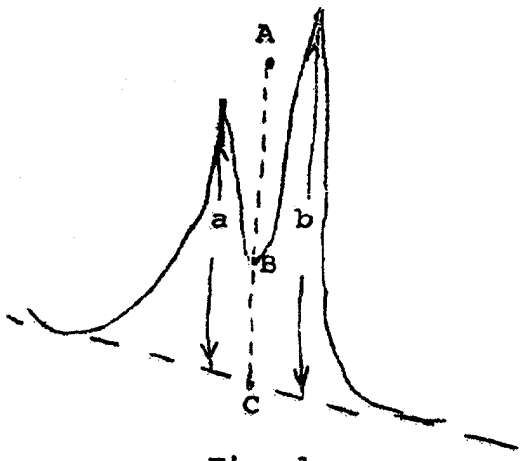

Fig. 1

It is simply the ratio of the distance from the lowest point of the valley B to the point A located at the average height of the two neighboring peaks from a common baseline, and the average height AC. When the ratio is multiplied by 100, the v.p. values of all products prepared in the present study fall between 30 and 80. The larger the v.p., the larger the primary pigment particle size. The validity of this assertion is based on comparisons of physical data obtained on pigments breached with various organic solvents.

By measuring the v.p.'s on a series of carefully breached samples prepared by F. L. Reig with variations in the amount of ODCB used as well as the duration and temperature of breaching, it became obvious that particle size growth occurs during the breaching operation. The data compiled in Table I show that when using the same premilled crude, which is itself very poorly crystalline, a series of breached products are obtained which show an increase in v.p. and % β-phase content when either the amount of organic solvent, the temperature or duration of breaching is increased. Moreover, all other things being equal, the larger the grown particles, the more dispersible the final product.

TABLE I

ODCB/ CPC	Temp. of Breach.	Duration of Breach.	v.p.	Surf. Area	% β	Strength vs.BT-449-D,TS97419 in Vinyl Rubout	5 cuts	15 cuts
.163	25°C.	22 min.	30.6	50	0	121	127	121
.163	25°	120	36.8	-	0	119	128	120
.163	95	127	49.6	-	1.8	102	123	116
.489	25	120	46.0	63	0	96	118	109
.489	95	15	47.1	-	0	91	108	106
.630	28	128	45.2	-	1.1	98	110	107
.630	90-98	15	56.1	-	1.4	88	110	107
.630	90-98	127	60.1	71	4.3	88	94	101

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Additional support for the proposed mechanism comes from the observation that the crystalline crudes used for pre-milling, which show surface areas of about 25 to 35 $m^2/g.$, are broken down in the milling operation to a nearly amorphous state of fine particles which are highly aggregated as shown by electron micrographs. Proper breaching of the high energy particles with various solvents yields crystalline products ranging in surface area from about 65 to 75 m^2/g. Solvents of higher potency were found to give products showing higher v.p.'s and % β phase content as illustrated in Table 2 for products derived from the same pre-milled crude.

TABLE 2

Breaching Solvent	v.p.	% β phase	Reference
ODCB	59.8	12.6	1869/12A
Perclene	50.6	4.1	1869/44D
CCl_4	42.8	0	1869/12B

The postulated mechanism of breaching is in agreement with the mechanism of breaching suggested earlier by K. Batzar and A. R. Hanke for polychloro CPC. However, unlike the behavior of polychloro CPC, semichloro CPC is not entirely phase stable, as is shown in Table 2, particularly when the breaching solvent is relatively potent and the chlorine content is not strictly controlled. Typical pre-milled plant lots from past production campaigns show substantial variability in chlorine content (Table 3) with some lots falling below the specified limits of 3.8 to 4.5%.

TABLE 3

Lot of Pre-Milled Crude	% Cl
773	4.3
848	2.9
851	2.0
852	3.6
856	3.9
865	4.1
893	3.4
896	3.8

In addition, the uniformity of chlorine distribution, although believed to be significant, is largely uncontrolled. Mass spectrographic analysis of a purified semichloro CPC containing 4.5% Cl shows the presence of two substituted CPC's; a mono and dichloro species of unknown ratio (monochloro CPC requires % Cl = 5.81). Since the semichloro CPC is prepared by the addition of a specified amount of 4-chlorophthalic acid to a phthalic anhydride charge, the effectiveness of mixing will have a bearing on the chlorine distribution (and possibly content) in the product which, in turn, will affect phase stability with respect to organic solvents. This problem has in the past been aggravated by using the same production vessels both for LC (chlorine-free CPC) and BB (semichloro CPC) interchangeably without cleanout in between.

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To insure an adequate chlorine content in the crude, the amount of 4-chlorophthalic acid used in the synthesis has been increased and an effort is being made in the plant to avoid admixing chlorine-free CPC with the crude in order to maintain the required chlorine content.

When using ODCB in the laboratory as the breaching solvent, substantial amounts of β-CPC are formed even when the chlorine content falls within the specified limits. However, as is shown in Table 4, under essentially identical breaching conditions, the amount of β-phase in the product increases as the chlorine content in the crude decreases.

TABLE 4

Lot of Pre-Milled Crude	% Cl	% in Product Breached with ODCB	Reference
865	4.1	12.6	1869/12A
853	3.9	15.5	1869/9A
554	3.6	19.7	1869/8B

Since the time of solvent-pigment contact is another variable which may affect the degree of phase conversion, it is understandable why the use of ODCB in the plant can lead to an uncontrollable generation of β-CPC. Some plant lots have actually shown amounts of β-CPC in excess of 30%, which probably accounts for their excessive greenness and weakness. Thus, although particle growth is the mechanism by which breaching proceeds, the growth must be restricted and controlled. Excessive or uncontrolled growth can lead to weak products. In this respect, ODCB is not the solvent of choice despite its high degree of chemical stability in the basic breaching medium.

2. Desirable Properties of Breaching Solvents

At this point, it might be in order to define the requirements of a good breaching solvent as determined in the present study.

a. Ability to grow pre-milled semichloro CPC from very small, high energy particles without, however, causing overgrowth or excessive β-CPC formation.

b. Ability to form and maintain a reasonably stable emulsion in dilute aqueous sodium hydroxide by means of an emulsifying agent and reasonable force of mixing.

c. Chemical stability in an emulsion with dilute (about 0.5%) sodium hydroxide.

d. Possession of as low a boiling point or as high a vapor pressure as possible for easy and complete removal from the pigment by steam distillation.

e. Non-toxicity and non-flammability.

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In view of the above requirements, ODCB is not an attractive choice for still another reason. Its relatively high boiling point (180-182°C.) makes its complete removal difficult and time consuming even on a laboratory scale. On a plant scale, ODCB was left on breached pigment on numerous occasions. Incomplete removal of the solvent makes additional physical changes of the pigment possible particularly in the drying step (180°F.). Changes such as additional particle size growth, phase conversion, and particle agglomeration are possible.

In order to demonstrate these effects, two laboratory breachings were run on the same pre-milled crude using Staybelite as the emulsifying agent but one was deliberately worked up without distilling off a substantial portion of the ODCB. The product from the latter experiment showed adequate strength by rubout but very poor dispersibility in vinyl both at 5 and 15 cuts on a two roller mill relative to the product obtained on complete distillation of the ODCB. The experiment was repeated with similar results. This product contained more β-CPC and had a somewhat higher v.p. than the product freed of ODCB. Of greater significance, however, was the extensive agglomeration which occurred in the product not freed of ODCB in the distillation step. As is seen in Table 5, the surface area of this product was low and electron micrographs showed large agglomerates not unlike those seen in the pre-milled crude although their crystalline nature was quite apparent. The fact that breaching had occurred was obvious from the v.p. and good rubout strength compared to that of the precursor pre-milled crude.

TABLE 5

ODCB Distilled	v.p.	% β	Surface Area	Strength in Vinyl of 5% CaSx Lakes 5 cuts	15 cuts	Reference
Completely	56.2	19.7	66	103	95	1869/5A
Incompletely	58.2	22.1	34	125	110	1869/5E

The degree of ODCB emulsion stability is still another reason which puts ODCB at a disadvantage relative to other solvents studied.

3. Emulsion Stability Considerations

Of the three solvents, ODCB, Perclene, and CCl_4, which have been studied in some detail, the first is the most and the last the least potent. This is apparent from the extent of particle size growth and α to β-CPC conversion (see p.4). The more potent the solvent, the larger the ultimate particle size and the higher the β-phase content in the product. Unexpectedly, when breaching under the same conditions of stirring, the product obtained on CCl_4 breaching which showed the smallest particle size also showed the best dispersibility in vinyl. This is contrary to established principles. Obviously, another factor was at work. In addition, it was shown repeatedly that the use of CCl_4 in conjunction with sodium Staybelite, used in breaching with ODCB, gave a product of poor dispersibility in vinyl. A closer examination showed that sodium Staybelite does not cause the formation

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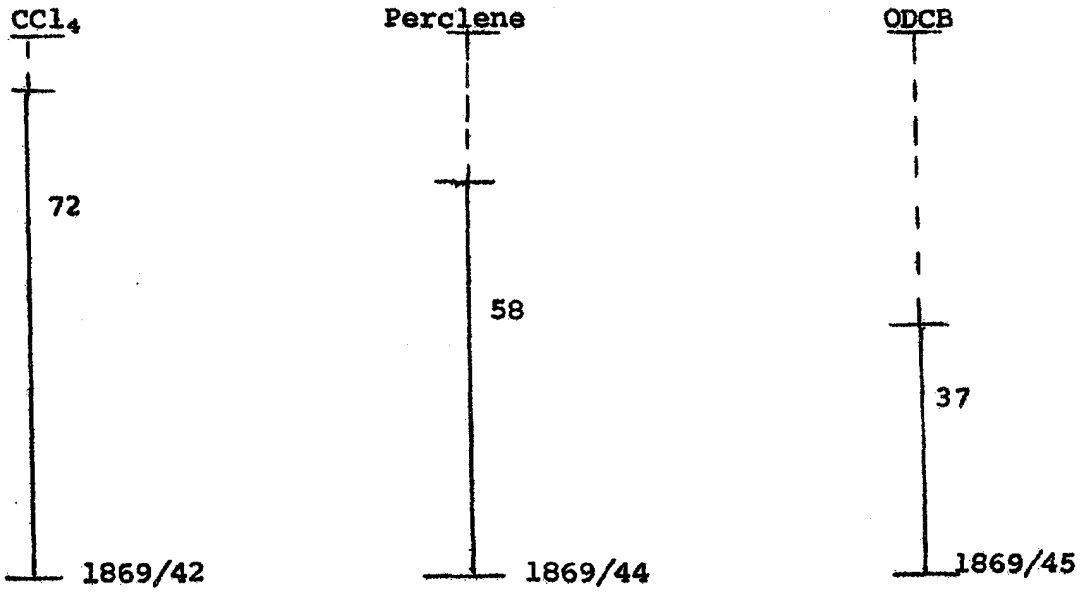
of a good emulsion of CCl_4 in dilute (0.5%) NaOH. Thus, to breach with CCl_4, a specific emulsifying agent was necessary, but more importantly it became apparent that the quality and/or stability of the emulsion in which the breaching is carried out has a bearing on the ultimate dispersibility of the breached product. Thus, a specific solvent is most effective with a specific emulsifying agent which forms the best possible emulsion. Moreover, the solvents themselves in the absence of water, though capable of growing the initially small particle pre-milled crude and generating β-CPC in varying degrees, give products of unusually poor dispersibility (1869/3). It is obvious that in a regular breaching, the growth and conditioning of the particles occurs at the solvent-water interface, the extent of which depends on the quality and stability of the emulsion. To demonstrate this point more convincingly, the quality of emulsions of ODCB and Perclene using sodium Staybelite as the emulsifying agent and CCl_4 in conjunction with Emcol P-10-59 were determined by taking photomicrographs of the emulsions as rapidly as possible after removal of a sample or, even more accurately, by the rate of settling or demulsification of the emulsions. Different quality emulsions, using the same ingredients, were prepared by conventional stirring and by high energy input in an Osterizer set at maximum speed. Breaching in all emulsions were carried out with conventional stirring. An examination of the final products dispersed in vinyl showed, without exception, for all three solvents, that breaching in an emulsion of greater stability yields a product of greater dispersibility. In addition, by comparing the three solvent-breached products with each other, it was obvious that CCl_4 gives the best and ODCB the least dispersible product. This is exactly the order of the stabilities of the emulsion prepared with equal energy input. The stabilities of the emulsions prepared with high energy input and measured by the degree of demulsification in calibrated tubes over a 12 hours period are illustrated below in graphical form. The stabilities are proportional to the length of the solid lines and on an arbitrary scale are 72, 58, and 37 for the three solvents shown. Viewed in another way, the broken part of the lines denote the degree of settling of the three emulsions.



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4. Breaching with CCl_4

As had previously been shown by F. L. Reig, G-3300 was an acceptable emulsifying agent for breaching pre-milled crude with CCl_4. In the present study, it has similarly been shown that the use of G-3300 affords good dispersibility products in the laboratory provided, in the absence of a laking operation, the acid-extracted product is washed with dilute ammonia (1869/9C,F). The latter removes some dark base-soluble impurities. The removal of similar base-soluble impurities is of even greater importance when breaching with solvents in conjunction with sodium Staybelite as the emulsifying agent. (See p. 15).

CCl_4 is a less potent solvent than ODCB and for this reason it consistently gave products of both lower v.p. and % β-CPC as is shown in Table 6.

TABLE 6

		Breached with ODCB		Breached with CCl_4	
Pre-milled Lot	% Cl	v.p.	%β	v.p.	%β
554	3.6	57.1	19.7	47.7	4.9
853	3.9	61.2	14.7	45.4	-
865	4.1	59.8	12.6	42.8	-

However, if the chlorine content in the crude fell below the recommended lower limit of 3.8% even CCl_4 was capable of forming a small amount of β-phase in the product. The low boiling point of CCl_4, its ability to form good emulsions and yield β-phase-free products, provided the chlorine content in the crude was kept at a sufficiently high level, were important advantages in favor of using CCl_4 as the breaching solvent.

After laboratory and Semi-Works demonstrations (F.L.Reig) that CCl_4 can be used as a breaching solvent when emulsified with G-3300, production was started in the plant. Although the dispersibility of most plant production was good, the performance was somewhat erratic and the products were red and dull vs. standard and at least the first 40-45 batches showed a substantial yellow migration in vinyl masstone (1% pigment). In addition, it was shown that the breaching tank was undergoing progressive corrosion. Expert opinion suggested that at the normal rate of breaching with CCl_4, the life time of the breaching tank and associated equipment was only one to two years.

5. Dispersibility of Plant CCl_4-Breached Products

Unlike the performance in the plant, laboratory experience showed that product of very good dispersibility could repeatedly be obtained. However, even laboratory products were redder and slightly duller than corresponding products breached with ODCB. The redness could be attributed to the formation of less or none at all of the β-phase in CCl_4 vs. ODCB-breached products.

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Since pigment dispersibility was shown to be a function of the emulsion stability, an obvious question arose; What kind of an emulsion is being used in the plant? To answer this question, two plant runs using CCl_4 as the breaching solvent were followed closely in a cooperative effort with Newport. The usual plant emulsion was prepared by recirculating the emulsion ingredients with a centrifugal pump in addition to the ordinary slow stirring in the tank. The earlier described methods of measuring emulsion stability showed the plant emulsions to be more stable than conventionally-prepared emulsions in the laboratory, but inferior to those made in an Osterizer. However, unlike the behavior in the laboratory, continued pump recirculation of the breaching mass during breaching appeared to cause or contribute to the breaking of the emulsion early in the breaching cycle. Following the failure of the emulsion, agglomeration of the pigment ensued which could be readily observed under the microscope. Simulation of this condition in the laboratory by using the same emulsion for two breachings but different energy inputs during breaching, caused the more vigorously agitated emulsion to break rapidly and yield a product of inferior dispersibility in vinyl (1869/53) relative to the product obtained on conventional stirring during the breaching process. Once again, pigment agglomeration which occurred in the rapidly stirred emulsion could be observed under the microscope and photographed. In addition, in one plant run, samples taken before and after breaking of the emulsion and worked up in an identical manner in the laboratory showed a definite dispersibility advantage for the former.

These findings suggest that the initial emulsion should be made with the greatest energy input to form as stable an emulsion as possible, but after the introduction of the pre-milled crude, the breaching be carried out with gentle stirring to avoid breaking of the emulsion. These changes were immediately incorporated into the process to the extent possible with available equipment. The results were quite satisfactory.

6. Migration in Vinyl and Hydrolysis of CCl_4

Although good dispersibility in vinyl and strength by rub-out are important requirements of BT-449-D, the pigment must also be free from migration in vinyl. Thus, any solvent or emulsifying agent used must not lead to substances in the pigment which will cause migration in vinyl. Still another important requirement of the breaching system is that it not be excessively corrosive to soft steel, the material of construction of the plant breaching vessel and associated equipment.

The cause or causes which led to migration in vinyl and corrosion of the equipment when breaching with CCl_4 were not immediately apparent. At first, it was assumed that the emulsifying agent G-3300 or its breakdown products were associated with the bleeding substance. However, direct addition of this agent to non-bleeding BT-449-D failed to produce migration in vinyl. To understand the possible effect of breakdown products, it became

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necessary to find the structure of G-3300. The producer of this agent, Atlas Chemical Industries, Inc., was reluctant to disclose full details concerning the structure. Based on partial suggestions of structure, IR spectrum, behavior with respect to base and elemental analysis, it was established that the agent (1869/13) is the isopropyl amine salt of dodecylbenzenesulfonic acid*. All salts of the sulfonic acid which could conceivably be formed and remain on the pigment, such as those of Cu^{+2} and Fe^{+3} were prepared and incorporated into non-bleeding pigment. The added salts failed to show migration in vinyl.

A clue to the migration as well as the corrosion problem was discovered when it was shown that two breachings of the same pre-milled crude with ODCB and CCl_4 in the same initial concentration of sodium hydroxide gave filtrates of different pH's at the end of the breaching procedure as shown in Table 7.

TABLE 7

Breaching Solvent	Initial pH	Final pH	Reference
ODCB	13.0	10.0	1869/9E
CCl_4	13.0	8.8	1869/9F

Although a decrease in pH was encountered with either solvent, it was repeatedly shown that the decrease was greater when breaching with CCl_4. A test for chloride ion in the final filtrates from the ODCB and CCl_4 breachings was negative and strongly positive, respectively. It was obvious that CCl_4 was hydrolyzing under the conditions of breaching. A review of the literature disclosed** that CCl_4 hydrolysis in aqueous mediumwas known and that the rate of hydrolysis is second order with respect to CCl_4 and is independent of hydroxyl ion and chloride ion concentration. It was clear that during the breaching operation, NaCl was being generated in the basic aqueous phase and HCl in the vapor phase.

$$CCl_4 + 4H_2O \longrightarrow 4HCl + CO_2$$

A close inspection of the plant vessel has actually shown a greater degree of corrosion above the liquid level than below it as might be expected on the basis of the effect of HCl vs. Cl^- on mild steel. The extent of CCl_4 hydrolysis in the aqueous phase could be ascertained by analyzing the final filtrates for chloride ion. Some analyses are given in Table 8.

*Based on the identity of IR spectra, behavior toward base and effectiveness in breaching it was shown that Emcol P-10-59, produced by the Witco Chemical Co., is identical with G-3300. The former is used extensively both at Newport and Newark and is less costly than G-3300. This information has been transmitted to Production.

**I.Fells and E.A.Moelwyn-Hughes, J.Chem.Soc. 398 (1959)

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TABLE 8

Breaching Solvent	Concentration of Cl^- in g/l.	Reference
ODCB	0.029; 0.038	1869/46
CCl_4	2.57; 2.74	1869/42

Since tap water used for breaching contained 0.008 g/l and the ODCB filtrates showed 0.03 to 0.04 g/l Cl^- ion, the difference arising most likely from impurities in the other breaching ingredients, the hydrolysis of CCl_4 generates (2.65 - (0.033-0.008)) about 2.4 g/l of Cl^- ion in the relatively short period (2-3 hrs.) of a laboratory breaching. The concentration of generated Cl^- ion in the plant was probably higher because of longer contact time, at high temperature, between CCl_4 and the aqueous phase*.

The occurrence of corrosion appears to have been directly linked with the migration problem. Many different pre-milled lots breached in laboratory glass equipment failed to show migration in vinyl. It had to be concluded that the corrosion of the interior of the plant vessel was somehow involved in the generation of the bleeding impurities. In addition, it was shown that migration of plant CCl_4 breached products became progressively less pronounced as the number of runs (about 45) increased although migration did not disappear altogether. It appeared likely that the corrosive effect of Cl^- ion on the wall scale which had accumulated over two decades of operations, as well as of the mild steel itself was giving rise to the migrating substances. Although the migrating impurities were not identified, it was shown that a standard CCl_4 breaching in a steel autoclave yielded a product which showed an unmistakable migration in vinyl. When the temperature of breaching in the autoclave was increased, the degree of migration also increased (1869/23). Upon adding some of the scale collected from the Newport vessel to a standard breaching in the steel vessel, a product was obtained which showed a strong migration in vinyl of the same color as encountered in plant production. Thus, the causes of corrosion and related migration have been identified. The excessive dullness of plant CCl_4-breached products may have been, at least in part, due to the generation of the migrating substance. It was clear that CCl_4 could not be used as the breaching solvent for the production of BT-449-D.

7. Perclene as Breaching Solvent

A new solvent for breaching which is more chemically stable than CCl_4 but less potent and lower boiling than ODCB, and one which forms satisfactorily stable emulsions had to be found. Several solvents were tried. Chlorobenzene in conjunction with sodium Staybelite gave a product of lower β phase content relative to ODCB (5.2% vs. 14.7%) and a lower v.p. (58.6 vs. 61.2)(1869/10)

*A plant-breached mixture (X-25) taken prior to CCl_4 distillation and stored at room temperature in a five-gallon kit for about six weeks showed a drop in pH from 11.8 to 2.5 and a very strong positve Cl^- ion test.

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but also inferior dispersibility in vinyl. Methylene chloride is far less potent than ODCB, but more potent than CCl_4 in terms of β-phase generation and particle size growth despite its low boiling point. Although considerably more hydrolytically stable than CCl_4 (1869/46B), its boiling point is much too low for handling in a plant operation.

Tetrachloroethylene, Perclene, was found to have a combination of physical and chemical properties including its ability to form adequately stable emulsions in dilute NaOH which made it a solvent of choice for the breaching operation.

Its chemical or hydrolytic stability was found to be substantially greater* than that of CCl_4 and essentially equal to that of ODCB, under the conditions of breaching. The greater hydrolytic stability of Perclene was apparent from the degree of lowering of the pH on breaching of the same pre-milled crude with CCl_4 and Perclene as shown in Table 9.

TABLE 9

Breaching Solvent	Initial pH	Final pH	Reference
Perclene	13.1	11.3	1869/44
CCl_4	13.0	9.1	1869/43

Breaching of the same pre-milled crude with the various solvents gave concentration of Cl^- ion in the final filtrates shown in Table 10.

TABLE 10

Breaching Solvent	Concentration of Cl^- in g/l	Reference
ODCB	0.034	1869/44
Perclene	0.041	1869/45
Perclene**	0.044	1869/58
CCl_4	2.6	1869/54

Perclene clearly shows a hydrolytic behavior similar to that of ODCB under the conditions of breaching. In addition, the boiling point of Perclene is 121°C., about 61° lower than that of ODCB making complete removal of the former from the pigment considerably easier. As a solvent for CPC, Perclene is considerably less potent than ODCB but more potent than CCl_4 as judged by % β-phase content and v.p. of laboratory-breached products derived from the same pre-milled crude at pigment to solvent ratios given in Table 11.

* According to Elchem, under a specific set of conditions, Perclene is about 2000 times more stable than CCl_4 with respect to hydrolysis in water.

**Semi-Works run 00272.

TABLE 11

Breaching Solvent	Pigment/Solvent	% β	v.p.	Reference
ODCB	1.92	12.6	59.8	1869/12A
Perclene	1.53	4.9	53.9	1869/44
CCl_4	0.63	0	42.8	1869/12B

A study to determine the optimum amount of Perclene to be used in the breaching operation gave best results at a pigment/solvent ratio of 1.23. The amount of Staybelite found to be satisfactory was 7.5% based on pre-milled crude which is 1.5% above the minimum required for optimum dispersibility (see p.15). Using these conditions in laboratory breachings, products of very good dispersibility and rubout strength were repeatedly obtained. A Semi-Works run (00272) based on laboratory determined optimum conditions and using a powerful recirculating pump for the emulsion preparation and a flash distillation unit for Perclene removal gave a product of very good dispersibility (superior to standard at 5 and 15 cuts in vinyl) and superior rubout strength (about 12% stronger) without requiring laking with calcium Staybelite. The product contained 2.9% β-phase and showed a v.p. of 51.6. Despite the higher amount of Perclene, the differences with the data given in entry #2 of Table 11 (products derived from same crude) are probably due to the short pigment-solvent contact time at high temperature in the flash distillation unit compared to that of a conventional laboratory batch distillation. The Semi-Works product was slightly redder but just as intense as standard.

Using Staybelite as the emulsifying agent and Perclene as the solvent, it has been shown in the laboratory that the pre-milled crude must show an extracted solid purity of 85% or higher. The lower purity pre-milled crudes cause early breaking of the emulsion with consequent impairment of quality. Although the nature of the impurities is not known, it has been demonstrated that inorganic salts will either decrease the stability or cause the emulsion to break. The reason for breaching in about 0.5% sodium hydroxide is that doubling the concentration (increase total ionic strength) in carefully controlled experiments had an adverse effect on quality, presumably due to a lowering in the emulsion stability. Other substances such as NaCl or alum (1869/36), the latter could conceivably be an impurity in pre-milled crude, were shown to have a similar deleterious effect on emulsion stability.

8. Perclene - Emcol P-10-59 Combination

Unlike the other solvents studied, Perclene is unique in that it can be successfully used for breaching with either Staybelite or Emcol P-10-59 as the emulsifying agents, the latter forming the better emulsion under the same conditions of agitation.

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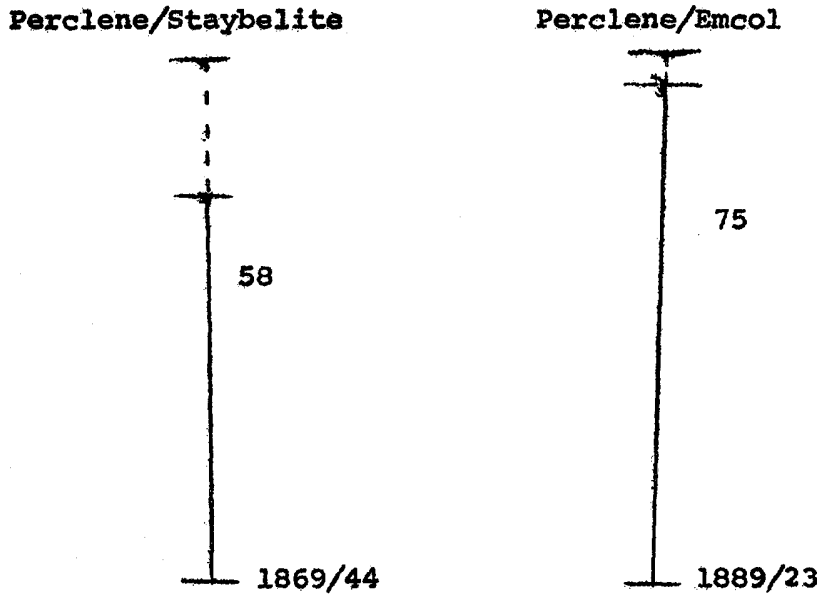
The greater stability of the Emcol emulsion was demonstrated by a comparison of the settling rates of two emulsions prepared with an equal concentration of emulsifying agents and power input. Below is given a graphic comparison of the emulsion stabilities.



The Perclene-Emcol combination gives the most stable emulsion. In agreement with this finding, marginally pure crudes (less than 85% purity) gave products of substantially better vinyl dispersibility when breached in emulsions prepared with Emcol P-10-59 rather than Staybelite (1889/23D). In addition, variation in the amount of Emcol used per unit weight of pigment causes less fluctuation in quality vs. similar changes in the amount of Staybelite (1889/19,21). Unfortunately, the ability of Emcol to form stable emulsions creates problems in filtration of pigment from basic solution which is the new mode of pigment isolation using Staybelite as the emulsifying agent (see p.15). Since the Staybelite process, as presently modified, is more economical and produces good quality product, there is no need, at present, for an alternative agent. However, should the need arise or should a better method of filtration be devised, Emcol could be considered as a possible alternative emulsifying agent.

9. Plant Breaching with Perclene

After the successful demonstration of the Perclene/Staybelite process in the Semi-Works, manufacturing was started in the Newport facilities. Although the stability of the Perclene/Staybelite emulsion produced in the plant was not as good as the

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one prepared in the Semi-Works (a more powerful pump was used at Newark) nevertheless in a ten batch campaign, seven batches showed vinyl dispersibility and rubout strength within shipping limits. The intensity of the products continued to be deficient relative to standard. In an effort to learn more about the process and obtain more consistent performance and improved intensity, several plant batches were followed closely in cooperation with F.L.Reig. It was shown that "in-process" samples including those taken prior to pressing worked up in the laboratory were in most cases stronger and more intense in vinyl and by rubout than the corresponding Newport lots and essentially equal to the quality of the Semi-Works product. Since the final steps of the process call for acid extraction followed by pressing, acid-free washing and press washing with dilute ammonium hydroxide, it was suspected that the final alkaline wash, which in the laboratory is known to remove Staybelite and other base-soluble impurities was not very effective in the plant. This was confirmed by demonstrating a significant improvement in quality upon extracting plant lot samples of inferior quality with dilute sodium or ammonium hydroxide, the former being more effective. Well base-washed or base-extracted products (1889/12) showed a 1.5 to 4.0% lower Staybelite content relative to the plant press-washed counterparts. In addition, it was shown that failure to base wash yields a product with a surface area of 50 m^2/g while an effectively laboratory washed or extracted counterpart showed a surface area of 70 m^2/g (1889/12). Thus, ineffective plant press washing leaves behind impurities including Staybelite which have a deleterious effect on dispersibility and intensity of product.

While washing of the acid-extracted product with proper press loads presents no problems, subsequent washing with dilute ammonia appears to reactivate the Staybelite present on the pigment causing the latter to peptize, and changing its washability characteristics. Channeling in the press is not an infrequent occurrence. Since proper press washing on the basic side appears to depend on the amount of Staybelite used in the breaching, an attempt was made to reduce the amount of the emulsifying agent. Unfortunately, substantial reduction of the Staybelite amount (1889/19) lowers the stability of the emulsion and causes a drastic decrease in the dispersibility of the product. The minimum amount required was found to be 6% on a pigment basis. Since the process calls for 7.5%, drastic reduction of Staybelite is, therefore, not possible.

One way to remove alkali-soluble impurities which unlike the press washing does not depend on chance, is to reslurry the acid-free washed presscake in hot dilute (1%) sodium hydroxide and carry out a bona fide extraction (1889/12F). The effectiveness of this approach has been demonstrated both in the laboratory and in the plant (plant lots X-12 through X-17). A closer examination of the plant process, however, shows that a more effective way to remove base-soluble impurities is not to precipitate them on the pigment by acidification in the first place and subsequently attempt a basic reextraction, but rather to press directly after steam distillation of the Perclene while all impurities are in basic solution in which the pigment is suspended. At this point in the process, the base concentration is slightly under 0.5% and can be

DUP050081293

increased to any desired level (1% is sufficient) and by heating nearly to the boil, any remnant of solvent can be eliminated and, in addition, the filtration facilitated (F.L.Reig). In the laboratory, this process offers no difficulties. In the plant, some difficulties of pigment bleed have been encountered particularly when applying high water pressure during the washing cycle. However, with manual wash-water pressure control, the last BT-449-D campaign (see attached batch card) was the most successful to date in terms of vinyl dispersibility, rubout strength, and intensity of product. Ten breaching lots from Newport were combined into eight acid extractions at Newark using about 1/2 lb. of H_2SO_4 per pound of pigment. The results are given in Table 12. The only problems encountered in this campaign had to do with yield and lot identity. It is noteworthy that the base-extracted material shipped from Newport does not settle in the drums and consequently does not require extra handling at Newark.

TABLE 12

Plant Lot	Npt.Lots of N-13	Est.No. of #	Yield of Ground Pigment	% Yield	Rubout*	Vinyl Dispersibility* 5 Cuts	15 Cuts
56370	46-48	2360	1775	75.2	$97R^{6}$	92	$96G^{6}I^{15}$
56406	43-44-45B	1422	1427	95.6	$98R^{4}D^{4}$	115	$103R^{13}D^{20}$
56455	45A-45B	2049	1862	90.9	$100R^{6}D^{8}$	99	$98\ I^{18}$
56625	49/52	2322	2340	100.8	$99R^{15}D^{15}$	110	$100R^{2}D^{2}$
56794	50A/54	2151	1155	53.7	$100R^{18}D^{20}$	97	$90R^{13}$
56889	51/50B/54	2300	1341	58.3	$93R^{12}D^{12}$	95	$90R^{13}$
56926	53/50B/54	2300	1936	84.2	$93R^{10}D^{13}$	100	$96R^{10}$
56970	47A/47B/47C/54	2300	1826	79.4	$93R^{6}D^{10}$	100	$95R^{10}$
		17274	12662	79.2%			

*Relative to standard lot 97419

The slight dullness shown in rubout requires comment. As stated earlier, breaching with Perclene yields products containing less β-CPC than the ODCB-breached counterparts (standard is ODCB breached). As a consequence, Perclene-breached products can be expected to be redder. It has been shown that the human eye tends to associate redness with dullness in CPC colors. Thus, blending of a BT-449-D sample breached with Perclene, which was read by Quality Control $96R^{12}D^{12}$ vs. standard, with 7% β-CPC (BT-383-D standard) has given a product which was read $97G^{6}I^{12}$ vs. standard and $100G^{12}I^{15}$ vs. the original BT-449-D sample (1889/27). Therefore, products from the new process can be expected to be somewhat redder and slightly duller vs. standard by rubout. For this reason, in the following campaign, products will be collected for setting up a new standard. After a new standard is set-up, products produced by this process can be considered for conversion to other existing codes such as BP-173-D, BT-425-D, and BT-413-D.

dc

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Approvals:
Opr.
[illegible]
[illegible]

Rev. 8/21/68
XOP-[illegible]
Batch/

BLUE B BREACHING (M-[illegible]-A)

1400# BATCH SIZE

(Perclene Breaching - Caustic Extraction)

Opr.	Instructions	Quantity Std.	Quantity Recorded
	CAUTION! ADD PROPER CHEMICALS IN CORRECT AMOUNTS AND SEQUENCE TO ELIMINATE HAZARDS.	Min. Max.	
	1. Check 28 still. Should be MT.		
	2. Add water to still, start agitator.	74" 75"	
	3. Start recirculating (2" valve open). Check recirculating line working. Supervisor must be present.		
	4. Add 3 pots of 50% caustic solution (15 gals.)	3 Pots	
	5. Agitate for 1/4 hour.		
	6. Check pH of still contents at lab; adjust to 11.5-13.0, if necessary. (11.5-13.0). 1 PT SAMPLE	pH 11.5-13.0	
	7. Close still manhole. Check to see that vapor line valve is closed and water is on condenser.		
	8. With agitator on, add Staybelite/Perclene.	105#/23"	
	9. Close 2" and open by-pass through orifice (1/2"). Recirculate 2 hrs.	2 hrs.	
	10. Sample 1 PT. emulsion at bottom of still. Give to Supervisor. Must pass 5-minute stability test.		
	11. Before charging pigment, close by-pass valve and recirculate through 2" line again as in Step 3.		
	12. Charge 1400# premilled BBZ (15 hrs.) over a one-hour period. (Approx. 1 Drum/9 mins.).	1400#	
	Lot #_____ Lbs._____		
	13. Agitate and circulate for 1/2 hour. Sample 1 PT. at bottom still valve. Give to Supervisor. Must pass 5-minute stability test.		

DUP050081295

Date	Time	Opr.	Instructions	
			14. Open by-pass steam two turns.	
			15. When still temperature reaches 40°C., close by-pass steam valve. Stop recirculating. Flush recirculating line and by pass with water.	
			16. Open valves for automatic steam control. Bring temperature to 50-53°C and hold for 2 hrs.	50-53°C
			17. After the 2 hours breaching, close steam valves to 28 still jacket. Make sure maximum water is on condenser. Cross connection to peerless pump line must be open.	
			18. Check 47B tank MT.	
			19. Add water to flash still accumulator with manual by-pass (3rd Flr.) valve to 60% of chart. Set LRC-10 on automatic control at this point.	
			20. One-half hour before hold period is up, turn steam on flash still very gradually to 18-20% of chart for 1200 lb./hr. steam. This will heat up all pipes before distillation. Set valves to return condensate to outside decanter. (Check rotameter for flow during heating up).	
			21. Open remote operated water valve (contains 1/8" orifice) to accumulator. Adjust FRC-9 manually at (4.5-5.5 psig air to valve) to drop 28 still level about 10"-15"/hr. If distillation is interrupted for any reason - close remote operated water valve to the accumulator and leave closed until distillation feed is resumed. THIS IS IMPORTANT or excessive water will accumulate in 47B tank.	
			22. Check the distillation every hour and record the following information. If the accumulator level begins to rise near the end of the cycle, reduce feed rate to hold constant. Start 47B agitator when 47B level reaches 36".	Time 47B Agitator starting

DUP050081296

Batch #

Date | Time | Init. | Instructions

22. (Cont'd)
Record data every hour.

	STILL POT			FLASH STILL	
Time	Level	Temp. °C.	Feed Lb./Hr. FCR-9	Steam FCR-3	47B Pr. Level

23. When distillation is nearing completion, a low level alarm will sound indicating low level in 28 Still.

24. Continue until 28 Still is empty. Close still outlet valve. Flush FV-9 valve and flash still with water.

25. Set FRC-9 manually at 0 air output to close feed control valve.

26. Wait 5 minutes, then turn off steam valve FV-3.

27. Add 3 pots of 50% caustic solution, then add water until level indicator just moves and pump directly to 47B by-passing flash still.

28. Drain accumulator by opening FV-10 (lower set point to 0). Flush with manual by-pass water valve to 30% and drain again. Close remote operated water valve (3/16" orifice) to accumulator.

29. Close still outlet valve.

30. Close high pressure steam valve outside. The distillation cycle is complete. Take 1 Qt. sample from 47B Tank. Have Control Lab check pH and check filterability of sample.

Lot #
Level and pH

Temperature
Time
(On Batch Card and Sample Label).

DUP050081297

XOP-[illegible]

Time	Opr.	Instructions	Min.	Max.
		EXTRACTIONS		
		1. Recheck and record pH in lab from 47B recirculation line. Should be 11.5-13. Take 1-Quart sample. If less than 11.5 add more of 50% caustic and recheck pH.	11.5	[illegible]

Estimated Total 50% Caustic
(For desired 1% NaOH Solution at 47B)

47B Level	Total 50% Caustic	Addition Req'd at 47B Lbs. Flake
47	31.5 Gallons	0
50	32.5	16
53	34.5	29
56	36.5	41
59	38.5	54
62	40.5	66
65	42.5	80

		2. If you smell Perclene in the sample, notify supervision.	Yes	[illegible]
		3. Check agitator on and heat to 90°C. Agitate 1 hour at 90°-95°C.	90°C	[illegible]
		PRESS OUT (57 PRESS)		
		1. Check 57 press clean and MT/. (32 Frames) Set up recovery system.		
		2. Pump charge to 57 press, fill press, Check tank MT.		
		Tank is MT. (Supervisor's initials)		
		3. Start washing.		
		4. Wash for 6 hrs. at 10-15 psi water pressure with warm (40°C) water. At the end of 6 hrs. check filtrate in lab for pH. ~~[illegible]~~ pH is high ~~[illegible]~~ IF continue to wash and resample every hour.	10.5-11.0	[illegible]
		5. Record total Hrs. washed. Final: Ohms ____ pH	10.5-11.0	[illegible]
		6. CHECK 60 MIXER MT		
		~~[illegible]~~		
		7. Dump press charge to 60 MIXER. Presscake full, firm or sloppy. If presscake smells of Perclene, inform your supervisor.		Full Firm Sloppy

DUP050081298

Instructions

8. [illegible] press chute with minimum amount of [illegible].

9. Close press, pressure test and repair [illegible] breakouts.

10. Mix one-half hour with recirculation [illegible] Check pH in [illegible]. Record pH. (Desired range [illegible]). WATCH FOR FOAMING. NOTIFY SUPERVISOR. MIXING TOO LONG MAY PRODUCE FOAMING AND SHUT DOWN IF NOT PACKED OUT IMMEDIATELY.

pH [illegible]

11. Start drumming from mixer.

12. Take two - 1 Qt. samples while packing out. Collect one dipper from feed of each drum when drum is approximately 1/2 full.

13. Record: Lot No. _____
Samples by: _____

No. of Drums	Net Wgt.	No. of Drums	Net Wgt.

Total Net. Wgt. _____

14. Stencil: N-13-A, lot, net and tare wgts. on each drum.

15. Flush mixer and recirculating line with water hose down sides.

MAKE-UP OF STAYBELITE SOLUTION (For one batch)

1. To mix tank on 3rd floor add [illegible]" (of gals.) Perclene. Take sample of Perclene to lab for specific gravity check. Record specific gravity here:

2. Add 10% of crushed Staybelite.

3. Stir for at least 30 minutes. Hold until ready for charging.

[illegible] NOT PACKED [illegible]ELY.

New Jersey Office Supply Co.

Filing Specialists

401 Frelinghuysen Ave., Newark, N. J.

PHONE BIgelow 3-0050

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