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NEWARK PLANT
PIGMENT COLOR RESEARCH REPORT

RESEARCH REPORT ON THE COLOR PROPERTIES OF
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NEWARK PLANT

PERMUT COLOR RESEARCH REPORT

Final Report

DEVELOPMENT OF PROCESSES FOR THE NEWPORT CPC PLANT
II - SYNTHESIS OF CPC

JUNE, 1945 - SEPTEMBER, 1948

CHARGE: A-11-C-229

SUBMITTED BY: E. B. Perkins

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INTRODUCTION:

This is the second in a series of reports dealing with the semi-works and plant development studies of processes for CPC manufacture at the Newport plant, carried out by the Chemical Division in the period 1946 - 1948. The first report (Reference 1) in this series summarized the results of studies of chlorophthalic acid manufacture; the present report is concerned with the investigations of the CPC condensation reaction, in which phthalic anhydride, chlorophthalic acid (for LB), urea, copper chloride and catalyst are heated together in kerosene to form copper phthalocyanine. The semi-works studies discussed in this report were carried out in the period June, 1946, thru May, 1948, while the plant work mentioned here was done during the initial operation of the Newport plant from April - September, 1948.

The work discussed here was carried out by Messrs. J.H. Baird, F.F. Ehrlich, R.D. Graham, O.J. Klein, J.W. Stagg, A.J. Stratton, and the writer, with the assistance of Mr. C.E. Collier of the Engineering Service Division during the development and the plant start-up studies.

ABSTRACT:

Copper phthalocyanine of yield and quality comparable to that obtained in the laboratory and semi-works, can be prepared in the Newport plant equipment by the use of the "LB" process. The results of semi-works and plant development studies on the CPC condensation reaction are summarized and the effects of variables on the process are discussed.

PATENT SITUATION:

The manufacture of copper phthalocyanine pigments by the "LB" process, involving heating together copper chloride, urea and phthalic anhydride with a catalyst is covered by a patent assigned to I.C.I. (Ref. 2). DuPont is licensed to operate under this patent. For a more detailed discussion of the patent situation, see Reference 3.

SUMMARY:

Study of the preparation of copper phthalocyanine in the Newark semi-works was started in August, 1946, using as the basic process the procedure developed in the laboratory (Ref. 4, 6). The method used in the initial semi-works preparations differed from that given in Appendix I only in that dry chlorophthalic acid was used in place of the presscake and all reactants were charged to kerosene in the reactor at room temperature, before the start of heating.

The equipment used in the semi-works studies was purchased in the used equipment market and was ill suited for the purpose, in addition to being in poor mechanical condition. These equipment deficiencies were a continuing source of difficulty throughout the semi-works studies and prevented the establishment of precise

operating cycles or definite standards for yields and pigment quality. However, with this equipment it was possible to establish the operability of the proposed process on a large scale, to demonstrate the successful use of chlorothallic acid prescald in the synthesis, to investigate various synthesis variables, and to prepare material in quantity sufficient for semi-scale study of the subsequent steps in the process.

The plant equipment for the CFC condensation reaction differed from that used in the semi-works in several respects, in addition to the matter of size: the agitator for the plant unit was quite different from the semi-works agitator in design and operation; the plant vessel was equipped with a nonious vapor eductor, whereas no such device was used on the semi-works unit; a urea melter was used in the plant but this device had never been operated successfully in the semi-works.

Numerous difficulties were encountered during the first few attempts to operate, in the plant, the CFC condensation process developed in the semi-works. A brief summary of the results of the first approximately 65 batches is given in Table I. The first attempt to carry out the reaction in the plant yielded apparently satisfactory quality pigment but the entire charge caked on the reactor walls because of excessive herosene losses and had to be removed from the vessel by hand. The second plant charge failed to react satisfactorily and yielded only a green-blue tar which had to be scraped by hand from the kettle; a total of six of the first 30 reactor charges (charges 102, 110, 112, 120, 124, 130) behaved in this fashion. In addition, the reaction was apparently only partially complete in three other instances, in which the product was obtained in the form of pellets which could not be pumped and were removed from the reaction vessel by draining the charge into drums. The difficulties at this stage of the plant development work were aggravated by failure of the reactor product pump to perform satisfactorily, by the inability to obtain a flow of molten urea from the urea melter, and by repeated failure of the heating unit for the plant reactor and various auxiliaries. Progress in correcting these difficulties was retarded by three fires, one of which caused failure of the glass lining of the reactor, necessitating a week's shutdown for repair, while another fire (due to lightning) rendered the entire plant inoperable for several days. The usual start-up difficulties involving leaking lines, pump failures, etc., and the necessity for continuation of construction work on the uncompleted parts of the building, complicated the situation.

Most of the plant mechanical problems were corrected as soon as manpower could be made available to do the necessary work. However, other problems were not so quickly solved. The difficulties in pumping the reactor slurry were reduced by converting the pump impeller from a closed type to an open one and by increasing the agitator speed in the reactor from 72 RPM to 90 RPM (charge 109) and later (charge 111) to 120 RPM, but this problem was not completely solved until the problem of incomplete reaction was overcome. (Subsequent experience indicated that a closed impeller would probably be satisfactory once the reaction problem was solved).

The urea melter continued to give difficulty for several weeks, necessitating revision of the process to provide for the use of the crystalline material rather than the molten product. The melter difficulties were finally overcome by reversing the direction of rotation of the melter agitator, providing heating for the unjacketed end of the mixer, using higher temperature steam for heating, and establishing a revised heating cycle.

Firing of kerosene vapors in the plant reactor was successfully prevented by the simple expedient of modifying the process so as to avoid the necessity for opening the reactor manhole while the kerosene in the vessel was hot, and by introducing inert gas (CO_2 or nitrogen) into the vessel before discharging it on completion of the reaction.

Foaming of the reaction mixture and the formation of an adhesive tar, rather than copper phthalocyanine, were the two plant problems which proved most difficult and required the longest time for solution. Neither of these problems had been encountered in either the laboratory or semi-works studies. Laboratory investigation indicated that production of the tar, rather than pigment, was a consequence of oxidation of kerosene. This observation was confirmed on both a laboratory and semi-works scale by additional work, which also indicated that foaming of the charge was magnified by such oxidation. The plant process was consequently modified so as to reduce the possibility of air oxidation: the temperature for addition of reactants - via the open manhole - to the kerosene was decreased, the length of time the manhole was open was kept at a minimum, a petroleum antioxidant was added to the kerosene, agitation of the kerosene in the presence of air was avoided as much as possible, and ammonium carbonate was added to the kerosene immediately upon opening the manhole to provide a blanket of inert gas over the liquid. Also, for a time following discovery of the aerial oxidation effect, only fresh kerosene was used as a reaction medium; for a period thereafter, a routine control synthesis was carried out on each batch of kerosene before use. (A procedure for conditioning oxidized kerosene for reuse, involving treatment with concentrated sulfuric acid, followed by centrifuging, was developed but was never put into plant operation.) Upon application in the plant of these measures to prevent oxidation, no further difficulties were encountered with failure of the reaction to proceed normally and foaming was reduced to within tolerable limits.

A great many variations in the process were tried in the plant during the period prior to discovery of the effect of air oxidation on the reaction. The results of these experiments, involving in many cases variation in the quantity and manner of addition of catalyst, the order of addition of reactants, the temperature and manner of addition of urea, etc., are open to suspicion. In the sections on the effects of variables which follow, an attempt has been made to indicate the magnitude of uncertainty introduced into the variables from these sources.

EXPERIMENTAL DETAILS:

Procedure

The semi-works procedure for the CPC condensation step in the preparation of LB type CPC is given in Appendix I; the procedure as originally specified for the Newport plant is given in II, while the Newport plant procedure as modified by experience gained during the "start-up" is given in Appendix III. The effects of variations in the standard procedure are discussed in a later part of this report.

Equipment

A simplified diagram of the equipment used in the Newark semi-works studies of the condensation reaction is given in Figure I. A diagram of the Newport plant equipment is given in Figure II. It is to be noted that, in addition to agitator design and construction details, the plant equipment differs from that used in the semi-works in that the plant unit is equipped with a noxious vapor eductor to draw off the fumes from the reactor, whereas such a unit was not incorporated in the semi-works design. The plant unit is also provided with facilities for adding molten urea to the reactor, whereas urea was added (in the solid state) by means of a star valve in the case of the semi-works unit. (A "urea melter" was installed in the semi-works but was found to be improperly designed and proved to be inoperable).

The semi-works equipment used for the semi-works synthesis of CPC prior to start-up of the Newport plant represented makeshift items obtained by purchase from the second-hand market and re-conditioned on the Newport plant. This unit comprised a 50 gallon glass lined reactor, equipped with a "home-made" steel agitator and provided with a "home-made" stainless steel cover with openings for a reflux condenser and other auxiliaries, and for introduction of raw materials; agitation was provided by means of a steel paddle type agitator driven at ca. 60 RPM. Heating was accomplished in the semi-works by circulating hot oil through the jacket of the reactor from an electrically heated oil bath; cooling was provided by circulating cool oil through the jacket. The semi-works vessel was equipped with a center bottom outlet comprising a two-inch cast iron nipple to which was attached a gate valve in a line leading to a centrifugal pump.

Following start-up of the Newport plant, a new 100 gallon glass lined reactor was installed in the semi-works. This unit much more closely simulated the Newport plant equipment than did the original semi-works unit on which plant design was based. Agitation comparable to that provided in the Newport plant was furnished in the new reactor by means of an agitator of design corresponding to that of the plant, and, in contrast to the original equipment, the new unit did not provide any opportunity for contact

of the reaction medium with exposed metal. Unfortunately, the new semi-works unit was installed too late during the plant start-up period to permit its extensive use, and only a very few reactions were carried out in it prior to completion of plant start-up.

The Newport plant reactor comprised a standard "Pfaudler" 1500 gallon glass lined reactor, equipped with a Schutte-Koerting noxious vapor condenser and other necessary auxiliaries, and heated by means of a Dowtherm unit. (See Figure II).

TABLE I : PLANT CPC SYNTHESSES DURING START-UP OF THE NEWPORT PLANT.

<u>Batch No.</u>	<u>Date</u>	<u>Remarks</u>
101	4/15/48	Crystalline urea added at 165°C (charge temperature). Difficulty with heating unit. Excessive kerosene loss. CPC product caked on reactor walls.
102	4/20/48	Crystalline urea added at 110°C. No CPC formed. Tarry product caked on reactor walls.
103	4/27/48	Crystalline urea added at 165°C. Charge caught fire but blaze extinguished. Apparently good CPC yield. This was the first charge which could be pumped from reactor.
104	4/30/48	Much trouble with urea melter. Mixture of molten and crystalline urea added at 135°C. Necessary to discharge blue (CPC) product to drums. Could not pump the reaction mass.
105	5/4/48	Urea heated for 11 hours before adding (molten) at 135°C. Much difficulty with reactor heating unit and with reactor discharge pump. Product blue (CPC).
106*	5/10/48	Molten urea (135°C) used. Kerosene fired, wrecking kettle. Charge O.K. (blue CPC) and pumped satisfactorily.
107	5/17/48	First charge in second kettle. Urea at 135°C. Poor reaction. Product in form of blue pellets discharged to drums from bottom reactor outlet.
108.	5/20/48	Urea at 165°C. Charge O.K. and pumped satisfactorily.
109.	5/22/48	Agitator speed increased to 90 RPM from 72 RPM. Urea added to hot (165°C) charge. Product O.K. and pumped with no difficulty.
110	5/24/48	Urea heated in melter 14 hours. Valve inoperable. Urea added at 150°C (charge temp.). Charge did not turn blue. Reactor cooled and tar removed by scraping.
111	5/28/48	Agitator speed increased from 90 RPM to 120 RPM. Procedure revised; copper chloride added at 145°C (charge temp.) instead of 110°C, followed by catalyst, then urea at 150°C. Good reaction, pumped O.K.
112	5/29/48	Procedure like 111 but difficulty with plugged kerosene line. No CPC formed. Tar removed by scraping reactor.

TABLE I - page 2

<u>Batch No.</u>	<u>Date</u>	<u>Remarks</u>
113	6/1/48	Procedure like 111 but "split" molten urea addition (20% at charge temperature of 160°C and 80% 160-180°C) and catalyst added in two portions (145°C and 160°C). Satisfactory product. Pumpable slurry.
114	6/3/48	Procedure like 113. Used fresh kerosene only. Satisfactory batch.
115	6/3/48	Procedure like 113 except molten urea added at 150°C and 155-165°C. (charge temp.). Used fresh kerosene only. Satisfactory batch.
116	6/4/48	Procedure like 115. Satisfactory batch.
117	6/6/48	Procedure like 115 except made with "used" kerosene. Satisfactory batch but slightly pasty.
118	6/7/48	Like 117. Satisfactory except could not pump. Drained from reactor.
119	6/8/48	Like 117. O.K. except difficulty with heating system and some trouble in pumping.
200	6/9/48	First batch of crude green base (Cl-free CPC). Made like 117 except no chlorophthalic acid used. Satisfactory. Pumped easily.
120	6/10/48	Like 117. No CPC formed. Tar scraped from reactor.
121	6/13/48	Like 115 (i.e. as 117) except only virgin kerosene used. Satisfactory. 200 gals. slurry left in reactor thru error.
122	6/14/48	Like 115 (same as 121). Satisfactory.
123	6/15/48	Like 117 (reused kerosene). Satisfactory.
124	6/16/48	Like 117. Satisfactory.
125	6/16/48	Like 117. No CPC formed. Necessary to scrape tar from reactor.
126	6/22/48	Like 115. (Virgin kerosene). Difficulty with urea heater so crystalline urea added with charge at 110°C. Third portion of catalyst added. Poor reaction. Product as blue pellets. Necessary to drain product to drums.
127	6/23/48	Like 115. Satisfactory.
128	6/24/48	Like 115 except made with "used" kerosene after steam distillation.

Table I - page 3

<u>Batch No.</u>	<u>Date</u>	<u>Remarks</u>
129	6/25/48	Like 115 except 50/50 mixture steam distilled and virgin kerosene. Third portion of catalyst added. Satisfactory product.
130	6/27/48	Like 129. No CPC formed. Tar scraped from reactor.
131	7/1/48	Like 115 except no water on eductor and kerosene heated in reactor instead of in head tank.
132	7/2/48	Oxidation effect discovered after 131. Control tests on kerosene started. Batch 132 made like 131 except third portion of catalyst used. No reaction until third catalyst addition at 199°C. Satisfactory product.
133	7/3/48	Like 131 except trouble with heating system. Satisfactory product.
134	7/5/48	Like 131. Satisfactory. Building fired by lightning 7/6/48. Shut down until 7/8/48.
135	7/10/48	Like 131. Trouble with heating system. Third portion of catalyst added. Satisfactory results.
136	7/13/48	All reactants except second portion of catalyst and urea added at 110°C; urea as in 115. Trouble with heating system. Product satisfactory.
137	7/15/48	Like 136 except urea added at 130°C. (charge temp.) and only one portion of catalyst was used. (added after urea). Satisfactory results.
138-146		Like 137. Satisfactory results in each case.
147	7/29/48	All reactants except urea added at 110°C. Urea at 130°C. Satisfactory batch.
148-157		Like 147. Satisfactory results.
202	8/10/48	Crude green base (Cl-free CPC). First CPC batch made with anti-oxidant for kerosene and use of ammonium carbonate. All reactants added at 110°C (charge temp.) except urea. Satisfactory results.
158-161	8/11/48 8/13/48	Like 202 except LB type CPC. Satisfactory results.
203	8/14/48	Crude green base (Cl-free CPC). Like 202 except made with previously used kerosene (First batch since 130 made with "used" kerosene.) Results satisfactory.
162		Like 203 except LB type CPC (use chlorophthalic acid).

*Molten urea added to all charges except where otherwise indicated.

Effects of Variables

The effects of various variables in the CPC condensation process are discussed in the sections which follow. It should be noted that many of the studies were carried out with use of equipment and procedures which differ appreciably from that which was subsequently adopted as standard and that the effect of oxygen on the reaction was not discovered until after completion of nearly all the semi-works studies and most of the work in the plant. An attempt has been made to assess the magnitude of the effect of these factors on the experimental results and to indicate the significance of the results presented here which were influenced in this way..

1. Type of kerosene

Semi-works runs were carried out with use of two different commercial types of kerosene and with samples obtained by fractionating a commercial grade of kerosene. Poor yields, 74% and 51% of theory, respectively, were obtained when a kerosene fraction with a boiling range of 195-225°C (obtained by fractionating "Deco" kerosene) was used in two reactions. The yield obtained in a control run made during this period using Dec-Baso was ca 85%. Previous laboratory experiments had shown the fractionated material to give yields comparable to those obtained with Dec-Baso. There is no obvious explanation for the difference between laboratory and semi-works results. The semi-works experiments were carried out under such conditions (All reactants mixed at room temperature before the start of heating) as was subsequently found to result in no serious air oxidation effects and hence are considered significant. Kerosene losses with the fractionated material (195-225°C) were appreciably greater than with the conventional type which contains a larger proportion of higher boiling materials (boiling range 190-275°C); no quantitative data are available regarding the losses, however. (These experiments with the low boiling kerosene were carried out with a view to the possible use of such material to simplify the problem of removal of kerosene from the reaction mixture by steam distillation.)

"Bayol D", an insecticide grade kerosene supplied by Standard Oil Company of New Jersey, which is lower in price than "Deco-Baso" brand kerosene which was specified (originally) was used in place of the latter material in 8 syntheses carried out in the semi-works (S.V. 40, 41, 42, 43, 44, 45, 92, 103). Serious caking in the reactor occurred in the case of four of these syntheses. "Bayol D" was found to be the equal of "Deco-Baso", insofar as yields and quality of the pigment obtained with its use are concerned, in the four syntheses in which serious caking was avoided. The tendency to caking in the reactor was much more pronounced with the Standard Oil product than with "Deco-Baso", apparently because of the greater losses of the former by volatilization during the synthesis step. It was concluded that "Bayol D" is a satisfactory substitute for "Deco-Baso" for the purpose in question if care is taken to avoid excessive kerosene losses or if sufficient kerosene is used to compensate for the losses. (It is believed that the

results of these experiments were not appreciably affected by oxidation of kerosene. Subsequent to completion of this experimental work, the use of "Royal D" has become standard plant practice.)

No experiments concerning the use of different commercial grades of kerosene were carried out in the Newport plant during the period covered by this report.

2. Variations in Quantity of Kerosene

Considerable variations were made in both semi-works and plant in the quantity of kerosene used as the reaction medium. No evidence was obtained that variations in this quantity had any effect on either pigment quality or yield so long as sufficient kerosene was present to provide adequate mixing of the reactants. For example, in the first synthesis carried out in the Newport plant, only a total of 670 gallons of kerosene was used for the synthesis with the result that the entire charge coked in the reactor. Despite the coking, the quality of the product was satisfactory and the yield was approximately 90% of the theoretical, which compared favorably with subsequent comparable syntheses made with 1200-1300 gallons of kerosene.

The optimum quantity of kerosene for use as a reaction medium is determined largely by the physical characteristics of the equipment used for the reaction, which greatly influence the magnitude of the losses of kerosene. This optimum quantity will undoubtedly vary with change in efficiency of the noxious vapor condenser, the heating system, etc.

3. Addition of Urea at Elevated Temperature.

Following demonstration in the laboratory that greater yields of GPC were obtained when urea was added to the hot reaction mixture, rather than to the charge before start of heating, this scheme was tried in the semi-works. No yield advantage which could be considered significant was evident in the semi-works as the result of this change. In view of the apparent yield increase obtained in the laboratory, with the possibility of some yield improvement in the semi-works, and also because of the evident advantage as regards decreased foaming, the addition of urea to the heated (165°C) charge was adopted as standard semi-works practice. Attempts to facilitate the addition of urea thru the use of molten material, rather than the crystalline product, were unsuccessful in the semi-works owing to solidification of the molten material in the cold transfer lines between the mixer and the reactor.

During the early stages of semi-works operation crystalline urea was added to the hot charge thru the open vent-holes with no major difficulties; subsequently, a star valve was installed for urea addition in the semi-works unit.

A great many variations in method of addition of urea were tried in the plant. There is much uncertainty attached to the results of these experiments since they were carried out for the most part without proper control of air oxidation effects. It was demonstrated, however, that a pigment yield of at least 85% of the theoretical could be obtained with addition of urea to the charge at temperatures in the range from room temperature (about 75°F) up to 180°F. It is not possible to specify an optimum temperature on the basis of the results.

Under the conditions used in the plant, molten urea was apparently fully as effective as the crystalline product, despite the fact that appreciable decomposition of urea undoubtedly occurs during its melting in the plant melter. It is possible that carefully controlled experiments may disclose a yield advantage to the use of the dry material; such an advantage - if any - would be expected to be less than 5%.

4. Agitation

The importance of good agitation of the reaction slurry during the OPC condensation reaction was demonstrated by laboratory studies of this step of the process: improved yield and better pigment quality was obtained when conditions were altered so that better agitation was obtained (Reference 5). Agitation was found to be no less important under semi-works conditions than in the laboratory. Inadequate agitation in the semi-works reactor was found to lead to poor yield and severe caking on the reactor walls, and possibly also brought about a decrease in quality. The effect of agitation changes were very forcibly illustrated by a series of syntheses in which agitator intensity was successively decreased owing to gradual wearing away of the steel agitator blades by corrosion and erosion. The yields (% of theory at dried crude stage) obtained over a period of 11.18 syntheses, during which the effective area of the agitator blade decreased to approximately one-half its initial value, after which a new agitator was installed, were as shown in Table II.

TABLE II - EFFECT OF AGITATION CHANGES ON PIGMENT YIELD AND CAKING OF PRODUCT IN RE. 6208 (SEMI-WORKS).*

<u>Semi-Works</u> <u>Batch</u>	<u>Yield</u> <u>(% theory)</u>	<u>Caking</u>	<u>Agitator Condition</u>
46	81.3%	None	Fair
47	78.2	Some	
48	83.0	None	
51	57.5	Severe	Badly corroded
54	63.3	Slight	" "
55	58.7	Some	" "
57	51.5	Severe	v. badly corroded (1/2 gone)
New Agitator after 57			
60	72.6	None	Good
63	84.6	In caking	"
65	84.6	In caking	Some corrosion

*In addition to agitation changes, certain minor variables entered into the batches in question. The effects of these latter variables is believed to be small compared to the agitation effects.

An attempt was made to determine the effect of very intense agitation on the CPC condensation reaction by carrying out the reaction in a vessel equipped with a patented high speed agitator of special design ("Covles Dissolver") intended to provide very intense agitation. (This work was done by Pigments Department personnel in the laboratories of the Covles Corporation, Cayuga, N.Y.) The agitation power input in the synthesis conducted with use of this agitator varied from 31 to 71 H.P. per 1000 gallons. It was observed that the maximum power (71 H.P.) was required during the initial heating period and that following the reaction at 195°C the power gradually decreased to the lower (31 H.P.) value. It was not possible to prepare a control with the usual agitative intensity in this case as the physical equipment available did not permit adjustment to the normal range of agitation. No quality or yield advantage was evident for the experimental product as compared to the usual semi-works material.

It is the writer's opinion that additional study of the effect of agitation variations on the condensation reaction is desirable. The fact that no advantages were evident, as the result of intense agitation in this particular experiment, is of doubtful significance in view of the since discovered marked effect of atmospheric oxygen on the reaction; there was excellent opportunity for contact of the reaction medium with the atmosphere in this experiment.

No conclusive data are available regarding the effect of agitation variations in the plant equipment. The rotational speed of the agitator in the plant reactor was increased from the initial value of 72 RPM to 90 RPM, and subsequently to 120 RPM, during the period of plant start-up. We do not know with certainty what effects resulted from these agitation differences; these changes were made during a period of considerable difficulty with the condensation reaction when the results were subsequently found to have been greatly influenced by the oxidation effects of atmospheric oxygen. It is believed - without definite proof - that the yield superiority of plant manufacture as compared to laboratory or semi-works performance, at the condensation stage, is a consequence of better agitation in the plant unit.

5. Water Content of Chlorophthalic Acid
(S.W. 33, 34, 35, 36, 37, 38, 39)

In the semi-works, pigment quality and yield were as good (within the experimental error) with undried chlorophthalic acid presscake (35-45% solids) as when the dried product was used. (Compare S.W. batches 23-32, made with dried presscake, vs batches 32-39 made with undried presscake.). A rather large number of syntheses were conducted under each of these conditions (dried chlorophthalic acid and undried chlorophthalic acid presscake of 35-45% solids) and while there were considerable variations in yield under each condition - apparently as a consequence of uncontrolled variables - a survey of the data indicate no differences in either yield or quality which reasonably can be ascribed to the use of the wet presscake rather than the dry material. The precision of the results is difficult to estimate with certainty; it is the writer's opinion that any yield effect is no greater than 5%.

Laboratory experiments showed that better yield is obtained, when wet chlorophthalic acid presscake is used, if the urea is added after the charge has been heated to an elevated temperature, rather than at room temperature. In all cases in the semi-works involving wet chlorophthalic acid presscake, in which yield data were obtained, the urea was added at an elevated temperature, which varied from 140°C to 165°C. A few semi-works syntheses were carried out with addition of urea with the presscake at room temperature. No yield data were obtained in such cases but it was established that pigment of the usual quality was produced.

All the plant CPC syntheses were carried out with undried chlorophthalic acid presscake. One attempt to obtain dried material for use in a plant CPC condensation reaction resulted in decomposition of the chlorophthalic acid because of excessive drier temperature (150°C). No further work was done in the plant on this matter.

6. Temperature of Addition of Chlorophthalic Acid.

The temperature of the charge at the time of addition of chlorophthalic acid presscake to the reactor was varied in the plant from 110°C to 150°C, and in the semi-works from room temperature (20-30°C) to 110°C - 150°C without effect which could be traced to this variable. It appeared to make no difference in the semi-works whether the other reactants were added at the time of addition of the chlorophthalic acid or in some other order. As previously noted, the precision of the results is not very great and it is possible that small, though significant, effects may have escaped our attention.

7. Effect of Rate of Heating

Reports from I.C.I. (Reference 7, 5) state that rate of heating of the reaction slurry to reaction temperature (195°C - 300°C) has an important influence on yield; rapid heating (< 4 hrs.) is reported to have resulted in higher yields than was obtained with slower heating (> 4 hrs.). No yield differences which could be considered significant were observed as the result of differences in heating rate in the work at Newark. (A difference of at least 5% in yield would be required in order to have been considered significant in the Newark semi-works.). In one instance (S.W.-26), in the semi-works, because of difficulty with the heating system, approximately 13 hours was required for heating to 195°C., in contrast to the usual time of 4-5 hours; the yield in the case of the more slowly heated batch was no less than that of the more rapidly heated product. No effect on pigment quality was observed at the result of variations in rate of heating under semi-works conditions. It is possible, however, that more carefully controlled experiments might reveal differences which were undetected at the time because of poor control of our evaluation methods, which were still under development at that time.

Similarly, the data do not permit of any precise quantitative conclusions regarding the effect of variations in rate of heating on yield or pigment quality in the plant. Relatively large yield and quality effects could have escaped detection in the plant because of inability to control satisfactorily the performance of the sulfation and extraction steps which precede quality and yield determinations, and also because of variations in the degree of oxidation of kerosene. The most definite statement which can be made on the basis of available information is that no large yield variations (in the writer's opinion greater than 15%) resulted from changes in the heating period even when this was increased from the usual 2-4 hours to as much as 8-1/2 hours. Quality effects, if any, resultant from differences in heating rate were apparently very small, since they were not detected by laboratory evaluation of the sulfated crude product.

It is conjectured that the yield effect reported by I.C.I. was associated with increased oxidation of kerosene as the result of long heating in contact with air; this oxidation effect, which was unrecognized at the time of the I.C.I. work, has since been shown to have a marked yield influence. It does not seem unreasonable, however, to predict that slow heating of the charge during certain temperature ranges would have an adverse effect on yield since urea is known to decompose rapidly at temperatures below that at which the formation of blue pigment is first detected; maintenance of such temperatures for long periods of time might conceivably result in decomposition of urea to products which would not yield CPC.

8. Effect of Oxidation of Kerosene

Six of the first 30 plant CPC condensation reactions carried out in the Newport unit yielded a brownish tar instead of the desired copper phthalocyanine slurry. The reaction mass in such instances solidified on even slight cooling below the reaction temperature of 195°C; it was necessary to dig the reaction product from the synthesis vessel manually in such cases. No such difficulty had been encountered at any time in the semi-works or laboratory. Investigation revealed that the difficulty was a consequence of oxidation of kerosene, either prior to or during the condensation reaction.* The difficulty was restricted to the Newport plant apparently because only that unit was equipped with an obnoxious vapor condenser which tended to draw a current of air thru the kettle, thus promoting oxidation. Conditions were particularly favorable for oxidation during the early part of the start-up period because of the practice at this time of opening the reactor manhole to permit addition of urea to the hot charge (the urea melter did not function satisfactorily at this time). With the manhole cover open, a strong current of air was pulled thru the kettle by the condenser.

Under the conditions originally prevailing at the Newport plant, the oxidation effect was apparently cumulative; a series of four or five good runs - with continued reuse of kerosene - was followed in some cases by a bad charge. (Table I). However, in certain instances, an "unreacted" charge was obtained even when fresh kerosene was used, sufficient oxidation apparently occurring during the heating to prevent the reaction from proceeding in normal fashion.

*This effect was discovered by means of syntheses carried out in open 250 ml beakers. A large number of such syntheses were carried out at Newport by the members of the Chemical Division start-up group, following which the oxidation effect was confirmed in the Newark laboratory and semi-works.

Oxidation of kerosene apparently occurred at several points of the process: (1) During standing in the underground storage tank. It is believed that the amount of oxidation which took place at this point was not serious. (2) During storage in the heated kerosene lead tank. In this case there was opportunity for considerable oxidation since hot kerosene (110°C) through which air was bubbled (from liquid level indicator) was in contact with a copper heater (copper tends to promote oxidation). (3) In the reactor. In this unit violently agitated hot kerosene was in contact with a rapidly moving current of air - induced by the noxious vapor condenser - during certain stages of the reaction as originally carried out. It was at this point that most of the troublesome oxidation apparently occurred. (4) During sulfation - which follows the condensation step - hot (110-120°C) kerosene was violently agitated in the presence of air.

The following physical changes were made in an attempt to minimize kerosene oxidation: (1) The liquid level indicator for the hot kerosene lead tank was activated by carbon dioxide rather than by air. (2) The manhole of the reactor was kept sealed as much of the time as possible. (3) The agitator was not operated except when necessary. (4) The water flow to the noxious vapor condenser was turned off entirely for a number of runs; this was not a satisfactory arrangement because of the resulting fume hazard, so a method of operation was devised providing for operation of the water jet only after sealing the manhole cover. (4) The temperature of addition of reactants thru the manhole was lowered.

In addition to these physical changes, a number of changes of a chemical nature were introduced. First, a small quantity (3 lbs. per plant batch) of a petroleum anti-oxidant, Paranox 441, was added to the kerosene immediately following the introduction of the solvent to the reactor. Second, A quantity (10 lbs. per plant batch) of solid ammonium carbonate was added to the kerosene immediately following its addition to the kettle and a like quantity was added to the sulfator before transfer of the charge to that unit was started. The addition of Paranox was decided upon following demonstration that under laboratory conditions kerosene (Dac-Baac) which had been heated to 195°C over a half hour period could be used successfully for a laboratory "beaker" synthesis if 1% of Paranox had been added prior to heating, whereas such heating in the absence of an anti-oxidant rendered the kerosene of no value for this use. The use of ammonium carbonate was based on the supposition that the gaseous thermol decomposition products of this compound would provide an inert "gas blanket" which would protect the kerosene by decreasing the opportunity for its contact with atmospheric oxygen. No tests were made to determine the effectiveness of this ammonium carbonate treatment in slowing the oxidation of kerosene. As the result of application of these steps, no further serious difficulties were encountered because of oxidation of kerosene, even with repeated reuse of the same kerosene.

During the course of these studies an attempt was made to establish the maximum permissible degree of oxidation of kerosene for the application in question and to specify oxidation limits in terms of a peroxide number. It was established that satisfactory results could be obtained with use of kerosene with a peroxide number of 2.6. The maximum permissible peroxide number for kerosene to be used in this reaction was not definitely established, however; it is the writer's opinion that the use of kerosene with a peroxide number greater than 3 is dangerous.

9. Foaming

No serious difficulty because of foaming was encountered in either the laboratory or semi-works syntheses. In the plant, however, foaming of the charge presented operating hazards and caused considerable yield loss in the case of several of the early batches. In these instances the foaming problem became acute upon addition of the initial portions of the molten urea to the hot charge (150-170°C) with a second stage frequently occurring when the charge temperature reached 185-195°C. Attempts to avoid this foaming behavior through the addition of urea (either molten or crystalline) at a lower temperature were unsuccessful, while very careful control of the rate of addition of molten urea was productive of some small benefit.

During the course of this difficulty various schemes were tried involving the addition of urea at various temperatures and under various conditions; none of these schemes produced any marked benefit. Also, during this period, considerable attention was given to possible means for capture and disposal of the material lost from the kettle by foaming. Action along this line was discontinued with discovery of the effect of oxidation of kerosene. The use in the synthesis step of severely oxidized kerosene, as previously noted, led to the formation of a tar rather than CPC, with little foaming, while the use of less extensively oxidized kerosene resulted in formation of CPC with severe foaming, and unoxidized kerosene yielded CPC without serious foaming. Following action to control oxidation of kerosene, the foaming problem was brought under satisfactory control. (It is worthy of note that while foaming was brought within tolerable limits so that under normal conditions the charge does not foam from the kettle, some foaming does occur within the vessel. An appreciable increase in batch size would be possible if foaming could be overcome completely.)

10. Catalyst Variations

The quantity of ammonium molybdate catalyst used in the first 39 semi-works syntheses (S.W. 1A, 1B - 25) was the amount recommended on the basis of prior laboratory work; this quantity (2.5 lbs. ammonium molybdate per Newport batch of CPC as outlined in Appendix) was subsequently recommended for the Newport plant.

This quantity was also used in a number of subsequent batches (S.W. 54, 55, 57, 58, 155, 168, 179, 180, 181, 243, and 247) but in most of the LB syntheses carried out in the semi-works after S.W.-25 and prior to plant start-up, the quantity of catalyst was increased by a factor of 1.75. (This corresponds to an increase from 2.5 to 4.5 lbs. per Newport plant batch.). Also, following plant start-up, several semi-works syntheses were made in which two additions of catalyst were used, each of which represented 5.0 lbs. per Newport plant batch. In no case was there any effect on either yield or quality which could be reasonably attributed to the effect of changes in catalyst quantity. Unfortunately, at the time most of this work was done, large variations existed from batch to batch because of variations in degree of air oxidation, so that only large effects could be detected.

In the case of the chlorine-free CPC syntheses, only one quantity of ammonium molybdate catalyst, corresponding to 2.5 lbs. per plant batch (Appendix II) was used in the semi-works.

In the plant, large changes were made in the quantity of ammonium molybdate catalyst and in the manner of addition of the catalyst. In certain cases as much as six times the usual quantity of catalyst (or $6 \times 2.5 = 15$ lbs. catalyst per batch representing 1000 lbs. of phthalic anhydride) was used in the plant. The catalyst was also added at various stages of the reaction and the total was added in several portions in a number of instances. This work was carried out during the period of plant difficulty and was based on the supposition that the failures to obtain satisfactory reaction in the plant were due to inhibition of catalyst activity or occlusion of the catalyst by solids in the reaction mixture. The results of these variations are not considered significant in view of the uncontrolled influence of kerosene oxidation on the results. Subsequently, satisfactorily controlled experiments were carried out in which it was found that a reduction in catalyst quantity from 5 lbs. per batch (twice the standard amount) to 2.5 lbs. produced no effect on yield or pigment quality. The effect of decreasing the amount of catalyst to less than the specified amount of 2.5 lbs. per batch was not investigated in the plant during the period covered by this report.

A number of semi-works experiments (S.W. 48-52, and 54-56) were carried out in which boric acid, with and without sodium hydroxide, was added to the reaction mixture, in addition to the usual amount of ammonium molybdate (see semi-works batches 48-58, 59, and 61-64). These experiments were conducted in syntheses of chlorine-free CPC as well as with the LB type. The primary object of the use of boric acid in these cases was to retard corrosion of the steel agitator, with another object being to obtain a yield increase. The results, which apparently indicate a yield decrease from the use of boric acid with the molybdate, are considered inconclusive because of inability to control agitation satisfactorily

during this series of experiments. It was necessary to replace the steel agitator during the series of runs because of extreme corrosion-erosion. There was no decrease in rate of corrosion of the steel agitator because of the use of basic acid.

The use of sodium hydroxide (2% of phthalic anhydride) in the reaction mixture has been reported by I.C.I. (Reference 8) to result in improved yield of chlorine-free pigment, and certain laboratory yields obtained at Newark also indicated as much as a 5% yield improvement from this source. (Other experiments indicated no yield improvement). The results of semi-works study (see S.W. 49, 50, 52, 56, 59, 61, 62) of this factor were inconclusive for reasons discussed previously.

11. Anhydrous Copper Chloride

One semi-works charge (S.W.-275) was made with use of anhydrous copper chloride (CuCl_2) instead of the dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) which is ordinarily used. There was no apparent quality advantage from use of the anhydrous material. The data do not permit of a conclusion regarding yield effects as there were appreciable yield losses in processing the material before yield determination.

12. Use of "Niagara" 4-chlorophthalic Anhydride

Two semi-works syntheses (148, 150), were carried out with use of chlorophthalic anhydride manufactured by Niagara Alkali Company. (At the time this work was done, consideration was being given to the possibility of using chlorophthalic anhydride supplied by this Company in place of chlorophthalic acid of our own manufacture.). The products obtained were quite green compared to the corresponding ones made with chlorophthalic acid of the usual quality, in agreement with results obtained previously in the laboratory. Because of this tinctorial difference, no further consideration was given to the use of the "Niagara" material. No yield data were obtained in these semi-works experiments.

13. Use of Trichlorobenzene (TCB) Reaction Medium (S.W. 119, 165, 175, 213, 216)

Serious consideration was given to the possible use of trichlorobenzene (TCB), rather than kerosene, as the medium for the CPC condensation reaction. This solvent (TCB), which is used by Orchem for this application, under laboratory conditions gave a product of better tinctorial quality than was obtained with kerosene, particularly when the pigment was separated from the reaction slurry by filtration followed by washing with fresh TCB. Semi-works synthesis S.W.-119 was carried out with TCB to determine the behavior of this solvent in the reaction under

semi-works conditions. No unusual difficulty was encountered other than those consequent on handling a toxic material (TCB) in equipment not designed for that purpose. The slurry was sulfated and most of the solvent was removed by centrifuging. The material centrifuged readily in a semi-works perforate basket centrifuge to yield a cake of 70-75% solids. The centrifuged CPC sulfate was then hydrolyzed and the solvent was steam distilled from the alkaline medium with a steam consumption of 16 lbs. per lb. of TCB. Both laboratory and semi-works grinds showed the product to be superior in intensity to any of the charges made in kerosene. Four additional semi-works syntheses were carried out to provide further information regarding the process. In all cases, the pigment obtained was superior in intensity to its kerosene counterpart. However, there was great variation in the character of the final synthesis slurry and in behavior of the pigment on sulfation. While the initial experiment indicated that the sulfation product did not settle sufficiently well to permit separation of the solvent by decantation, it was possible to separate a considerable proportion of the solvent in this way in subsequent runs and it appeared that a process based on this type of solvent separation might be developed for plant use.

Major attention during this period was concentrated upon solvent separation through use of a device such as a filter. It had been demonstrated in the laboratory that some of the intensity superiority of the TCB material was due to the solubility in this solvent of by-product impurities which are not soluble in kerosene, and separation of the solvent from the pigment in such a manner that these impurities were removed with the solvent led to improved intensity. It was established that the pigment, as the sulfate, could be separated from the solvent by either centrifugation or filtration. An attempt to carry out filtration of a semi-works batch to provide data for filter design was not completely successful since the sulfated slurry could not be pumped from the reactor. However, the product was transferred to the filter by means of buckets, where it filtered satisfactorily and was washed with two 50 lb. portions of TCB (40-50 lbs. of CPC). The product obtained on hydrolysis and steam distillation of the hydrolyzed sulfate was quite "rubbery" and could not be pumped. Nevertheless, a portion of this material finished in the laboratory yielded a pigment of excellent tinctorial quality.

At the time of this work, a final choice of reaction medium for initial plant operation became necessary in view of the imminent start-up of the Newport plant and the urgency of concentrating all our efforts on one process. On the basis of the information available at that time, kerosene was chosen in preference to TCB, the principal reasons for the choice being the economic advantage of the kerosene process because of the greater yield and lower solvent cost, the greater experience of the group with that process, the much greater toxicity of TCB as compared to kerosene, and the greater difficulty encountered in the semi-works with solvent recovery with use of TCB.

The relative merits of the TCB and kerosene processes, as demonstrated by the limited amount of work done at Newark, may be summed up as follows:

- (1) TCB yields the more intense pigment.
- (2) TCB gives a more fluid slurry so that less difficulty is encountered with agitation and reactor discharge.
- (3) The kerosene process has an appreciable economic advantage since the cost of TCB is much greater than that of kerosene - on either a volume or weight basis - and the loss (lbs.) of TCB in the Newark trials was at least as great as with kerosene. Also, on the basis of Newark laboratory studies and information from Orchen, the higher yield (5-10%) is obtained in kerosene. (No semi-works yield data were obtained at Newark for the TCB process because of the extreme difficulty of obtaining the data under the conditions of the experiments).
- (4) TCB is much more toxic than kerosene and special consideration must be given to this matter in equipment design.
- 5: The limited amount of information available indicates that air oxidation effects are much less important with the TCB process than when kerosene is used.

It appears that it may be necessary to re-examine the TCB process in the event that pigment of optimum intensity is required.

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2. U.S. Patents 2,197,453 and 2,214,477. Wyler to ICI.
3. KN-46-54. Final Report. General Patent Survey. Phthalocyanine Pigments. July, 1946. Newark File 223.4.
4. KN-47-5. Chlorine-Free CPC: Synthesis by Phthalic Anhydride - Urea - Kerosene Method. February, 1947. Newark File 223.4.
5. KN-46-7. Review of ICI Phthalocyanine Art. A digest of ICI reports in DuPont Company Files. March, 1946. Newark File 223.4.

6. KN-47-51. "Monastral" Fast Blue LB: Laboratory Process Studies. February, 1948. Newark File 223.4.
7. ICI Report E-3644. Copper Phthalocyanine. Preparation by the Solvent Process. July, 1938.
8. ICI Report E-6392. "Monastral" Fast Blue E: Preparation by Solvent-Urea Process in Presence of Caustic Soda. December, 1949.

APPENDIX I

Semi-Works Procedure for Synthesis of CPC.

To the semi-works 50 gallon glass lined reactor, add, at room temperature, the following reactants in the order shown:

218 lbs. (34 gal.) of kerosene (Note 1)

Start agitator, then add

40.5 lbs. (see Note 2) phthalic anhydride.

0.22 lbs. (100 grams) of ammonium molybdate (Note 3)

13.7 lbs. of copper (II) chloride dihydrate (Note 4)

Heat to 110°C (circulate hot oil thru reactor jacket)

To agitated slurry at 110°C, add

11.5 lbs. (see Note 2) 4-chlorophthalic acid (100% weight) presacake.

Close reactor and heat charge to 165°C with agitation and add over a 45 minute period, via a stir valve, continuing heat and agitation during the addition

73.5 lbs. crystalline urea.

Heat the charge to 195°C and hold at $195 \pm 5^\circ\text{C}$. for four hours, then cool the reaction mass to 150°C (by circulating cold oil thru the reactor jacket) and pump it to the sulfator (steam still).

NOTES

1. "Leo-Baso", a deodorized insecticide grade kerosene, supplied by L. Sonneborn Sons, Inc., was used in the semi-works runs, except where otherwise indicated.
2. The quantities of phthalic anhydride and chlorophthalic acid were such as to give a mol. ratio of phthalic anhydride/chlorophthalic acid = 82.7/17.3. The quantity of phthalic anhydride added was adjusted as necessary to compensate for the unchlorinated phthalic anhydride (as phthalic acid) present in the crude chlorophthalic acid. The quantity of crude chlorophthalic acid presacake added is sufficient to yield 11.5 lbs. chlorophthalic acid. National Aniline or Monsanto phthalic anhydride was used in the semi-works studies.

3. The quantity of ammonium molybdate ordinarily used in the semi-works was twice that specified for the plant. J. T. Baker's CP ammonium molybdate was used.
4. The quantity of copper chloride dihydrate is adjusted as necessary to compensate for variations in water content. For example, during most of the semi-works runs this quantity was increased to 15.0 lbs. because of excessive water content of the material. Harshaw's technical grade copper chloride dihydrate was used in the semi-works studies.

APPENDIX II

Original (Newport Plant Start-up, April, 1948) Plant Procedure for Synthesis of CP2.

To reactor at 110 - 125, add

540 gals. (3500#) of kerosene at 110°C (Note 1)

Start agitator and add to the reactor

one batch chlorophthalic acid presscake (Note 2)

Then add to reactor

279 lbs. copper chloride dihydrate (Note 3)

797 lbs. phthalic anhydride (Note 4)

2.5 lbs. ammonium molybdate (Note 5)

Close reactor manhole and heat agitated charge to 165°C during 60 minutes by use of Dowtherm. To agitated charge at 165°C add over 45 minutes

1500 lbs. urea (molten) at 132-135°C (Note 6)

Heat charge to 195°C (with agitation) as rapidly as possible (estimated 2-2.5 hrs.). Hold charge at 1950 ± 3°C for 4 hours (continuing agitation), then pump it to the sulfator. Flush reactor with

100 gals. of hot (110°C) kerosene and pump the flush to the sulfator.

NOTES

1. The temperature difference between the kettle and the kerosene should not be greater than 65°C. to avoid cracking of the glass kettle lining. Since the kettle will ordinarily be hot (from previous synthesis) hot kerosene is used.
2. The quantity of chlorophthalic acid presscake added was such as was calculated from semi-works experience to give a mixture of 1.17 mols of 4-chlorophthalic acid with a total of 5.58 mols of phthalic anhydride and unchlorinated phthalic acid, when mixed with 797 lbs. of phthalic anhydride. The plant plans provided for the use (on an unanalyzed basis) of one plant batch of chlorophthalic acid per synthesis charge. Each chlorophthalic acid batch was estimated to contain -

325 lbs. (1.17 mols) 4-chlorophthalic acid.
30 lbs. (0.20 mols) unchlorinated phthalic acid.

The addition of 797 lbs. (5.38 mols) of phthalic anhydride to the chlorophthalic acid batch was calculated to yield the desired mixture of 1.17 mols of chlorophthalic acid with 5.58 (5.38 + .20) mols of unchlorinated phthalic anhydride and phthalic acid. The mol % of chlorophthalic acid in the mixture was calculated to be $100 \times 1.17/6.75 = 17.3\%$.

3. Harshaw's technical grade copper chloride was used. The material was analyzed for water content and in those instances in which the analysis differed significantly from the theoretical (21.1% water) the quantity of copper salt was adjusted accordingly.

4. Commercial grade phthalic anhydride was used on an "as is" basis. See also Note 2.

5. J.T. Baker's technical grade ammonium molybdate was used on an "as is" basis. The quantity specified for the plant was only one-half that used in most semi-works experiments. Experimental studies at Newark had shown such a reduction to be possible.

6. DuPont's urea was used. It was specified that heating for a longer period and at a higher temperature than the minimum required to melt the urea was to be avoided in order to minimize thermal decomposition of the material.

APPENDIX III

Newport Plant Process for Synthesis of CFC as of September, 1948.

To the glass lined 1500 gallon reactor add

7130 lbs. (1100 gallons of Deco-Bass kerosene at 110°C (Note 1)

Start agitator and add via the kettle manhole

10 lbs. ammonium carbonate (Note 2)

3 lbs. Paranox 441 (Note 2)

Close manhole and heat kerosene to 110°C
by means of Dowtherm.

With agitator running, add via the manhole
(The chlorophthalic acid presscake vs mixed ("dredged")
with a portion of the phthalic anhydride)

one batch of chlorophthalic acid presscake (Note 3)

835 lbs. of phthalic anhydride (Note 3)

Then add

285 lbs. copper chloride dihydrate (Note 4)
and follow with

5 lbs. ammonium molybdate (Note 5)

Heat charge (with agitation) to 150°C (Note 6)
and add over 45 minutes, continuing heating
during addition

1500 lbs. molten urea at 135-138°C.

Heat charge to 195°C and hold at 195°C for 4 hrs.
(Slurry is agitated throughout the entire period).
At the end of the digestion period at 195°C
add to the sulfator

5 lbs. ammonium carbonate

Pump the slurry to the sulfator.
Flush the kettle with

1300 lbs. (200 gals.) of Deco-Bass kerosene.

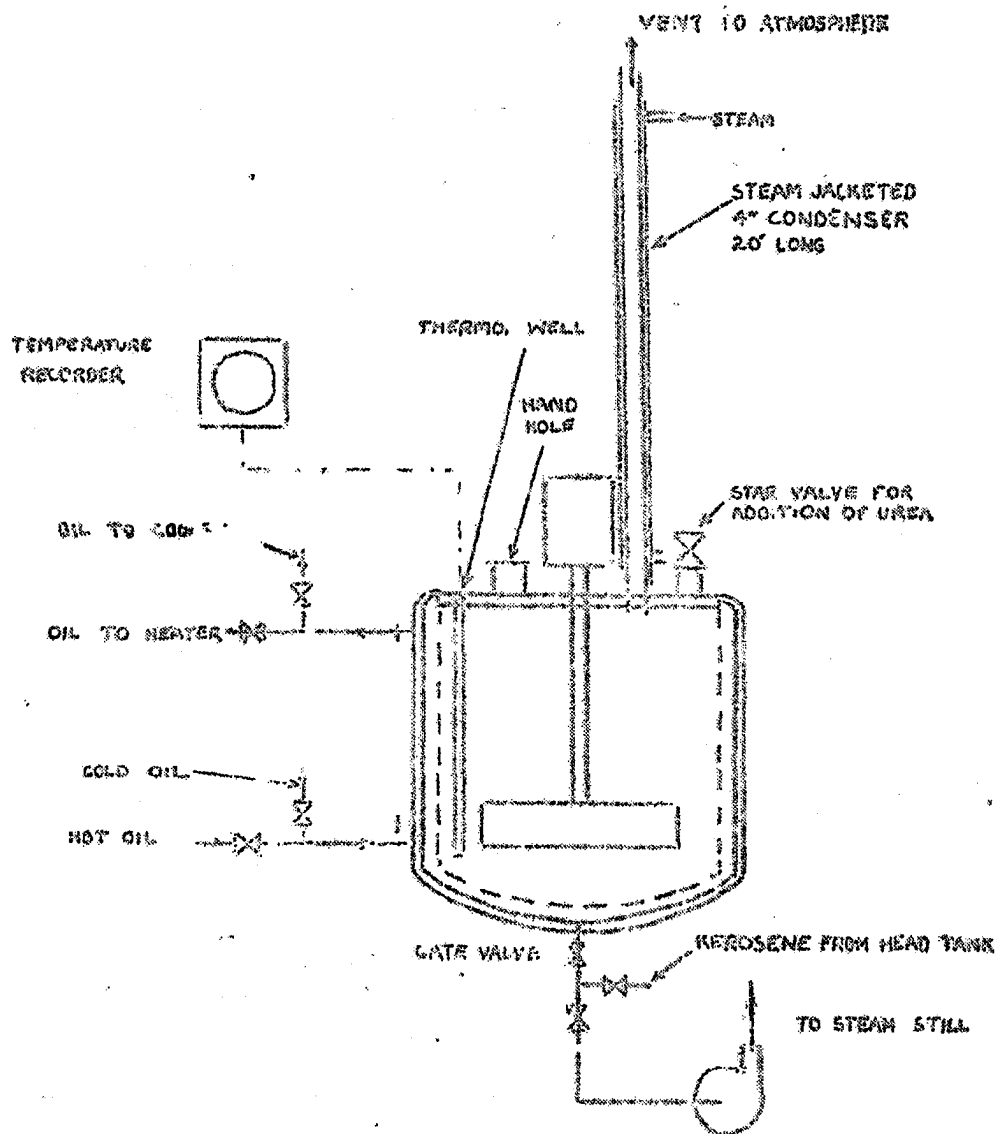
NOTES (Appendix III)

1. The temperature difference between the kettle and kerosene should be no greater than 65°C; a greater temperature difference is likely to result in cracking of the glass lining of the kettle. Since the kettle will ordinarily be hot from the preceding synthesis, hot kerosene is used.
2. The purpose of the ammonium carbonate is to provide an inert gas blanket (by thermal decomposition) and thereby decrease the extent of oxidation of kerosene at this point. Paranox 441 is an anti-oxidant for petroleum and is also used to retard oxidation of the kerosene.
3. One batch of chlorophthalic acid - prepared from 236 pounds of phthalic anhydride - is added for each synthesis charge. This quantity was found to give, with 835 lbs. of phthalic anhydride, approximately the desired mixture of 1.2 moles of chlorophthalic acid with 5.6 moles of unchlorinated phthalic anhydride. The chlorophthalic acid is used without analysis. The quantities of phthalic anhydride used for chlorophthalic acid preparation and for the synthesis were changed from that originally specified (Appendix II), since it was found that under plant conditions more than the expected yield of chlorophthalic acid was obtained.
4. The quantity of copper (II) chloride dihydrate was increased from the 279 lbs. originally specified to 285 lbs. to compensate for the excess water usually found in this ingredient. The original plant practice of analyzing the copper chloride for water content was discontinued and 285 lbs. of the "as is" dihydrate was used in each synthesis.
5. J. T. Baker's technical grade ammonium molybdate/used on an "as is" basis.

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FIGURE I

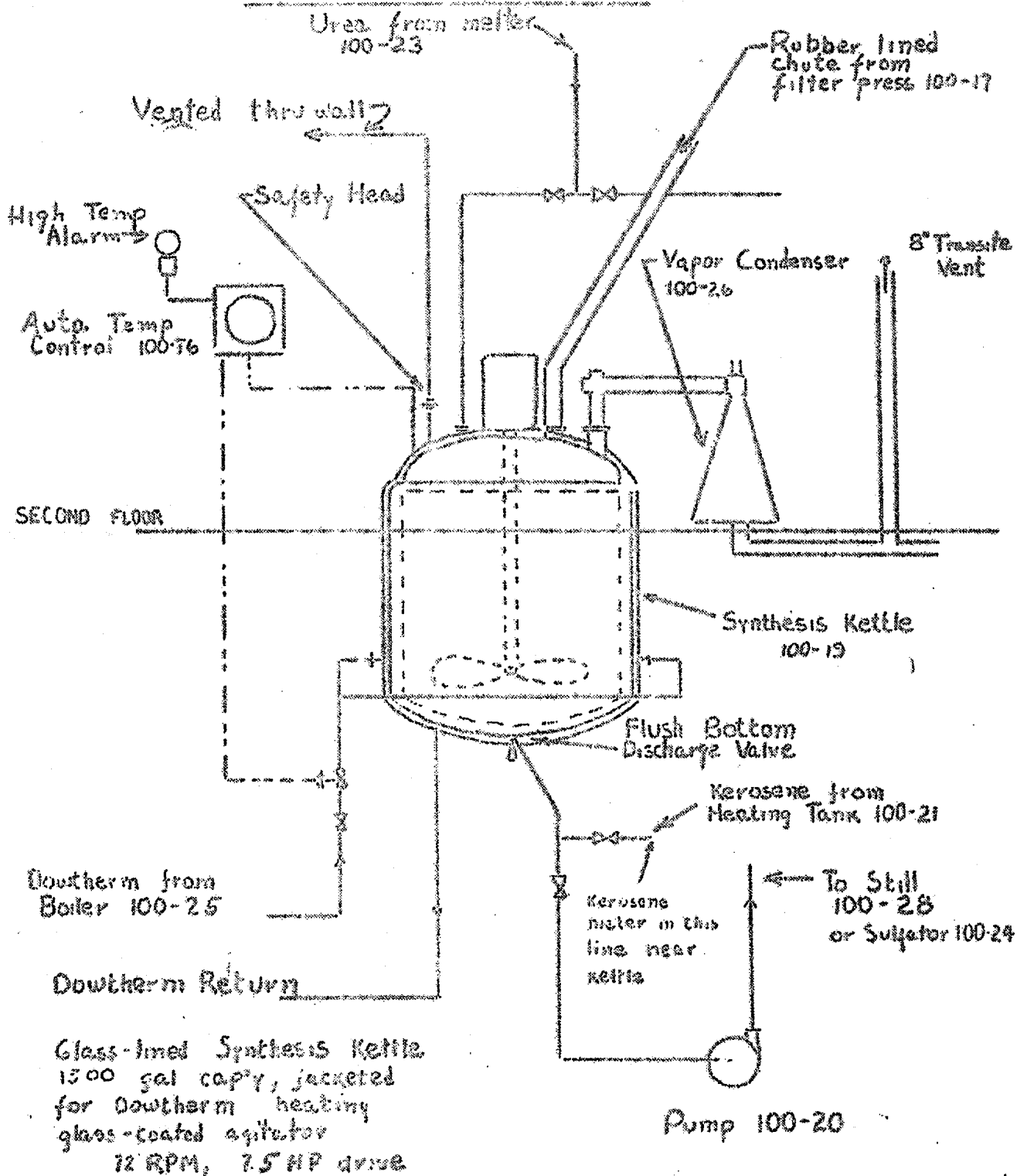
SEMI-WORKS CPC SYNTHESIS EQUIPMENT



SEMI-WORKS GLASS-LINED REACTOR
50 GAL. CAPACITY, JACKETED, OIL HEATED,
STAINLESS STEEL AGITATOR AND COVER

FIG. II

NEWPORT PLANT EQUIPMENT SYNTHESIS CRUDE CPC



NOTE - THE EQUIPMENT IS SHOWN AS OF TIME OF PLANT START-UP. CHANGES WERE MADE SUBSEQUENTLY IN CONDENSER SYSTEM, PIPING, AND UREA ADDITION FACILITIES.