STUDIES IN THE ALKALI FUSION REACTIONS FOR THE PREPARATION OF VAT DYES

A THESIS

SUBMITTED TO

THE UNIVERSITY OF BOMBAY

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

(in the faculty of Technology)

BY

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POONA-8

May 1968

to
the memory of
RENE' BOHN
(1862 - 1922)
whose outstanding discovery of INDANTHRONE
at the turn of the century heralded an era
of brilliant, fast dyes for cotton.

to
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(1885 - 1955)
whose outstanding discovery of INDANTHRONE
at the turn of the century heralded an era
of brilliant, fast dyes for cotton.

Statement required to be submitted under Rule 0.413
of the University of Bombay

No part of this work has been submitted for a degree or diploma or other academic award. The literature concerning the problems investigated has been surveyed, and all the necessary references are given. The experimental work has been carried out entirely by me. In accordance with the usual practice, due acknowledgement has been made whenever the work presented is based on the results of other workers.

Poona
15th May 1963

V. N. Iyer
Candidate

Professor B. D. Tilak
Research Guide

CONTENTS

SUMMARY AND CONCLUSIONS

Indanthrone, a commercially important vat dye and blue pigment, is prepared by the alkali fusion of 2-aminoanthraquinone, usually by employing a mixture of sodium and potassium hydroxides and an oxidising agent at about 200-20°. The patent literature describes additions of various chemicals to assist the fusion reaction and increase the yield of the dye. But even under the most favourable conditions the maximum yield of the dye is only about 55% (by weight).

A critical examination of the large number of methods reported in the patent literature has revealed the fact that indanthrone had been obtained in varying yields. The information available on the alkali fusion of 1-aminoanthraquinone and on the continuous alkali fusion, however, claim higher yields of the dye.

The other important vat dye, dibenzanthrone, is manufactured by the alkali fusion of benzanthrone in the presence of fluxes like sodium acetate, solvents such as naphthalene, and anthracene residues (free from carbazole). Here also the literature records variety of modifications of the alkali fusion process using different additives.

An extensive survey of the literature reveals the absence of systematic studies to predict the effects of various process variables on the yields of indanthrone and dibenzanthrone.

SUMMARY AND CONCLUSIONS

A detailed study was undertaken of the alkali fusion of 2-aminoanthraquinone and benzanthrone with the following main objectives:

1. to establish the effect of different process variables such as time, temperature, proportion of the reactants, isolation of the product on the preparation of indanthrone in batch reactions;
2. to study the effect of the addition of surface active agents such as alkyl phenols, fatty alcohols and alkali-stable anionic and non-ionic surfactants during the alkali fusion in order to economise the process;
3. to repeat the study of the effect of the surface active agents in the alkali fusion of benzanthrone to dibenzanthrone with a view to economise the use of naphthalene flux;
4. to optimise the process conditions for the preparation of indanthrone by a statistical design;
5. to fabricate a continuous alkali fusion apparatus and assess the feasibility of its use in the preparation of indanthrone.

The considered variables in the production of indanthrone and dibenzanthrone which affect the optimum yield are evaluated to be 1. time of reaction, 2. temperature of reaction, 3. weight ratio of mixed caustic alkali to 2-aminoanthraquinone,

4. weight ratio of the surface active agent to 2-aminoanthraquinone, and 5. weight ratio of sodium hydrosulphite to 2-aminoanthraquinone in the case of indanthrone; and 1. time of reaction, 2. temperature of reaction and 3. weight ratio of naphthalene flux to benzanthrone in the case of dibenzanthrone respectively. The experiments were designed statistically and the results were analysed by the method of canonical transformation as proposed by Box and Wilson to find the optimum conditions. For the evaluation of the first order effects, a fractional factorial design was used and the second order effects were found out by adopting a suitable design.

The above-mentioned objectives were achieved to some extent during these investigations. The yields of indanthrone and dibenzanthrone both of excellent tinctorial strength were of the order of 55 and 85% (by weight) respectively.

One of the main objectives of these investigations was to determine the technical feasibility of using a continuous reaction assembly for the alkali fusion. The patent literature refers to a solitary attempt to make use of a continuous reactor system in which a yield of 65.9% of indanthrone (commercial strength) is claimed. The continuous reactor assembled by us consisted of an overhead reservoir for molten alkali of 3 litres capacity which discharged the melt into a measuring device which fed known quantity of the alkali melt into the reactor. The 2-aminoanthraquinone is fed by a screw-conveyor designed for this purpose. The reactor, in the shape of a 'V' contained two stirrers in both arms which

were driven by two independent quarter H.P. electric motors. The product was discharged from the left arm of the 'V' which was collected and analysed.

The data collected from the batch alkali fusion reactions for the preparation of indanthrone were employed in the semi-continuous fusions. Measured quantities of 2-aminoanthraquinone mixed with sodium phenolate and molten alkali mixture were fed to the 'V' reactor at the time intervals of 5, 15 and 30 minutes respectively. Ten such runs constituted one batch in the semi-continuous reactor. The product of each batch was separately isolated and the yield and strength were estimated. Under optimum conditions a yield of 52% (by weight) of indanthrone (130 strength as compared to commercial 100 strength product) was obtained.

A study with nearly 50 runs have indicated that a semi-continuous reactor system of this type can be used for the alkali fusion reaction and its technical use appears feasible.

Introduction

Alkali fusion reaction is useful for effecting a variety of condensation reactions, particularly where ring closures are involved. Some of the examples of these are the synthesis of indigo from phenyl glycine or its ortho carboxylic acid, the preparation of indanthrone and dibenzanthrone from 2-amino-anthraquinone and benzanthrone respectively. The prime necessity of this reaction is the exclusion of water in the reactants and also to remove the water formed in the reaction immediately, in order to obtain good yields of the products. This is carried out by a variety of means such as the addition of sodium amide or quicklime, by working under vacuum, passing through a stream of some indifferent gases or by removal of water with the help of solvents (1).

Sodium hydroxide is normally used as the alkali as it is less expensive. However, there are quite a few cases where good results are obtained only with potassium hydroxide which also melts more readily and is more active than the sodium hydroxide. Sometimes mixtures in varying proportions of both hydroxides are used because of the still lower melting points of such combinations.

The molten alkali can exert an oxidising action. This is illustrated by the fact that anthraquinone-2-sulphonic acid does not yield the 2-hydroxy derivative, but alizarin in alkali fusion. This can be enhanced by the addition of suitable oxidising agents.

A highly reactive alkaline reagent is prepared by mixing caustic potash with ethanol or methanol (2). This reagent acts as a substitute for molten caustic alkali in effecting alkali fusion reactions.

The caustic alkali used in the reactions should not contain excess of water. In the case of indanthrone, for example, the yield of the dye is considerably decreased and the formation of by-products like alizarin increased with increase in water content in molten alkali (3). The proportion of unaltered 2-aminoanthraquinone is also increased with the water present.

Chemistry of indanthrone

History (4, 5)

The present century started with an important discovery in the field of vat dyes when Rene' Bohn synthesised indanthrene blue in 1901 by the alkali fusion of 2-aminoanthraquinone. Bohn, in an attempt to prepare a blue analogue of indigo, studied the cyclisation of the condensation product of 2-aminoanthraquinone and monochloroacetic acid using caustic alkali, and obtained a blue dye, which was named 'indanthrone'. Later, Bohn obtained the same dye by alkali fusion of 2-aminoanthraquinone itself, which was therefore not an indigoid dye. The new dye synthesised had the constitution of dihydroanthraquinoneazine, which was later confirmed by Scholl and co-workers.

The discovery of indanthrone stimulated interest in the field of fast vat dyes for cotton which were hitherto unknown. Intensive research was undertaken on anthraquinone chemistry, resulting in the synthesis of a variety of complex ring systems of both carbocyclic and heterocyclic classes which involved new methods of condensation and cyclisation reactions especially the Scholl condensation using anhydrous aluminium chloride.

Classification of indanthrone (4, 5)

The characteristic structural unit is substituted anthraquinone. The parent ring system is known as phenazine or simply as azine, although the systematic nomenclature should be dibenzopyrazine. (Formula I, chart I).

Mechanism of formation of indanthrone and by-products in alkali fusion

Since the discovery of indanthrone by Bohn, several theories have been put forward to account for its formation by the alkali fusion of 2-aminoanthraquinone. Rene' Bohn, in his original synthesis, prepared indanthrone from 2-aminoanthraquinone by fusion with caustic potash. Flavanthrone (5, 13-didehydro-8, 16-flavanthrene dione) and other impurities were also obtained. When an oxidizing agent was used in the fusion, indanthrone was formed with other impurities except flavanthrone, but with a reducing agent at high temperatures, flavanthrone was formed (6).

Bohn considered that, as 2-hydroxyanthraquinone gave alizarin when it was fused with potassium hydroxide, the 2-aminoanthraquinone should also yield 2-amino1-hydroxyanthraquinone, and then indanthrone as a result of dehydration (7). But Scholl and Eberle showed that 2-amino-1-hydroxyanthraquinone was not an intermediate in indanthrone formation (7). They believed that the intermediate (II) might be a precursor of indanthrone but it was shown that the formation of indanthrone from (II) could be only by use of strong acids. They further suggested that the enolic form of 2-aminoanthraquinone (III) on formation would combine with 2-aminoanthraquinone itself to yield the adduct (IV), from which indanthrone would result by enolisation, addition, and finally oxidation (chart I). The imine-addition hypothesis was adopted by Barnett who regarded 2-amino-1 : 2'-dianthraquinoylamine (IX) as the most probable intermediate in indanthrone formation. Maki observed that when 2-aminoanthraquinone was added to molten potassium hydroxide, it yielded a violet melt from which 2-aminoanthraquinone itself was regenerated by addition of water, the changes being reversible. This action was catalysed by the addition of phenol (7) (see chart I).

The mechanism of the formation of indanthrone along with alizarin and flavanthrone was explained on the basis of p-quinonoid form of 2-aminoanthraquinone (8). According to Tanaka (9) the carbonyl group in 2-aminoanthraquinone had a great influence on the formation of indanthrone. Fusion of 2-aminoanthraquinone with alkali at 150-70° in the presence of an oxidising agent gave equal amounts of 1-hydroxy-2-amino-anthraquinone and a green compound, indanthrene B which

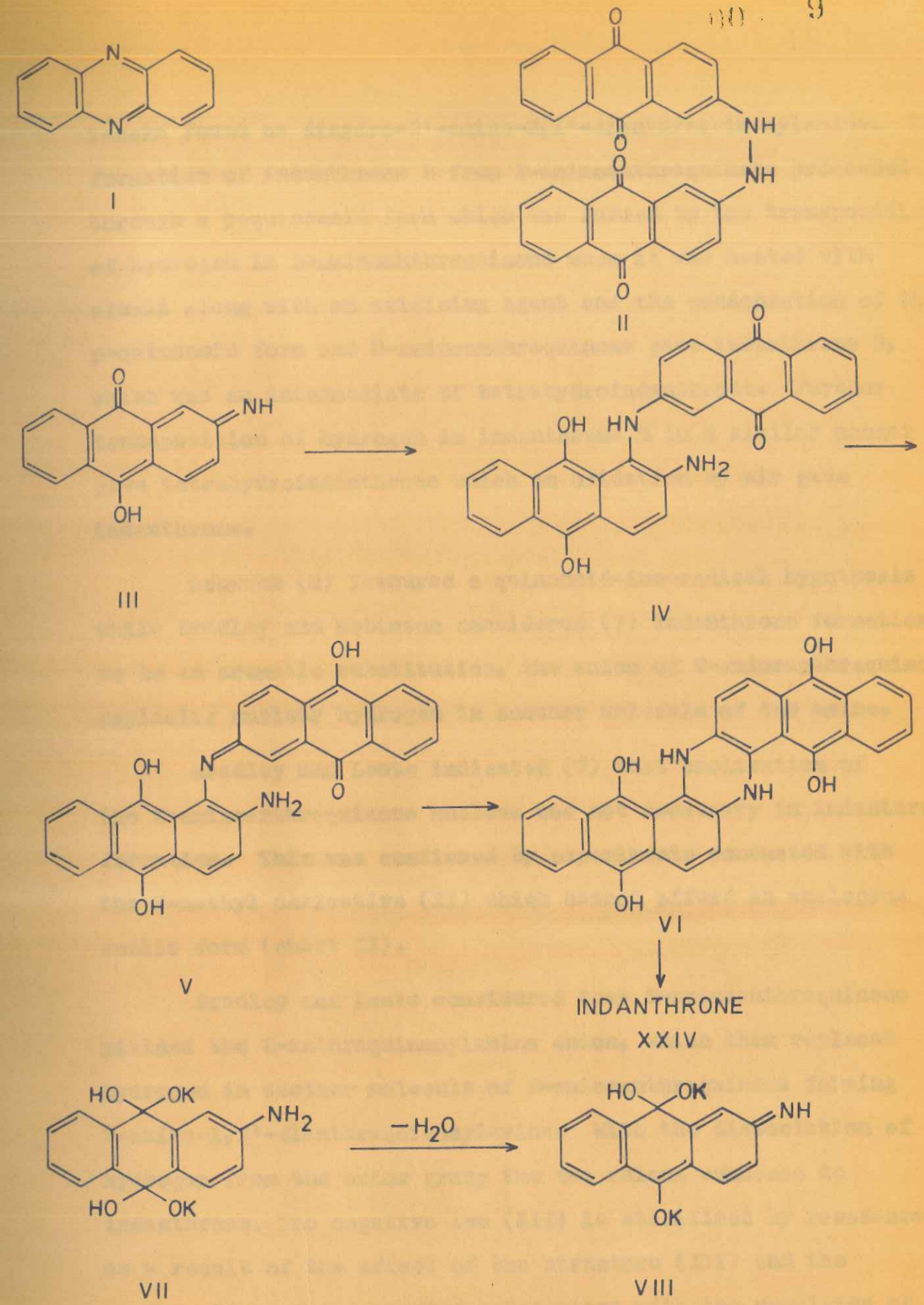


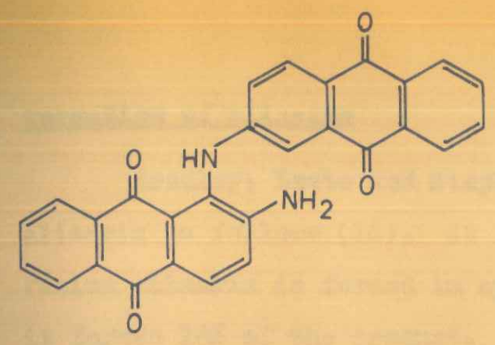
CHART – I.

Tanaka found as dihydro-2'-amino-2,1'-dianthraquinonylamine. The formation of indanthrene B from 2-aminoanthraquinone proceeded through a p-quinonoid form which was formed by the transposition of hydrogen in 2-aminoanthraquinone when it was heated with alkali along with an oxidising agent and the condensation of the p-quinonoid form and 2-aminoanthraquinone gave indanthrene B, which was an intermediate of tetrahydroindanthrone. Further transposition of hydrogen in indanthrene B in a similar manner gave tetrahydroindanthrone which on oxidation by air gave indanthrone.

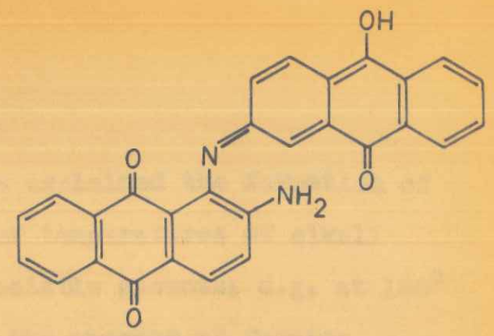
Schwenk (8) favoured a quinonoid-ion-radical hypothesis while Bradley and Robinson considered (7) indanthrone formation to be an aromatic substitution, the anion of 2-aminoanthraquinone replacing nuclear hydrogen in another molecule of the amine.

Bradley and Leete indicated (7) that enolisation of the 2-aminoanthraquinone nucleus was not necessary in indanthrone formation. This was confirmed by experiments conducted with the N-methyl derivative (XI) which cannot afford an analogous enolic form (chart II).

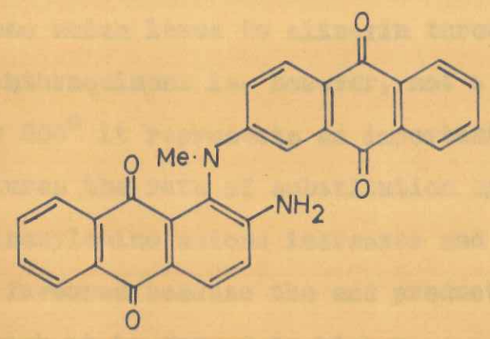
Bradley and Leete considered that 2-aminoanthraquinone yielded the 2-anthraquinonylamine anion, which then replaced hydrogen in another molecule of 2-aminoanthraquinone forming 2-amino-1,2'-dianthraquinonylamine. With the dissociation of hydrogen from the amino group the two anions condense to indanthrone. The negative ion (XII) is stabilised by resonance as a result of the effect of the structure (III) and the condensation of indanthrone takes place with the repulsion of a proton.



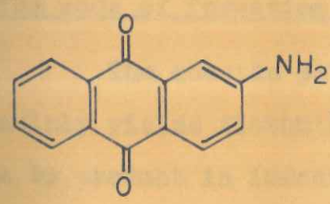
IX



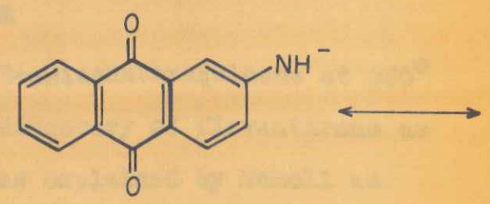
X



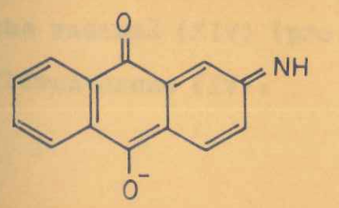
XI



XII



XIII

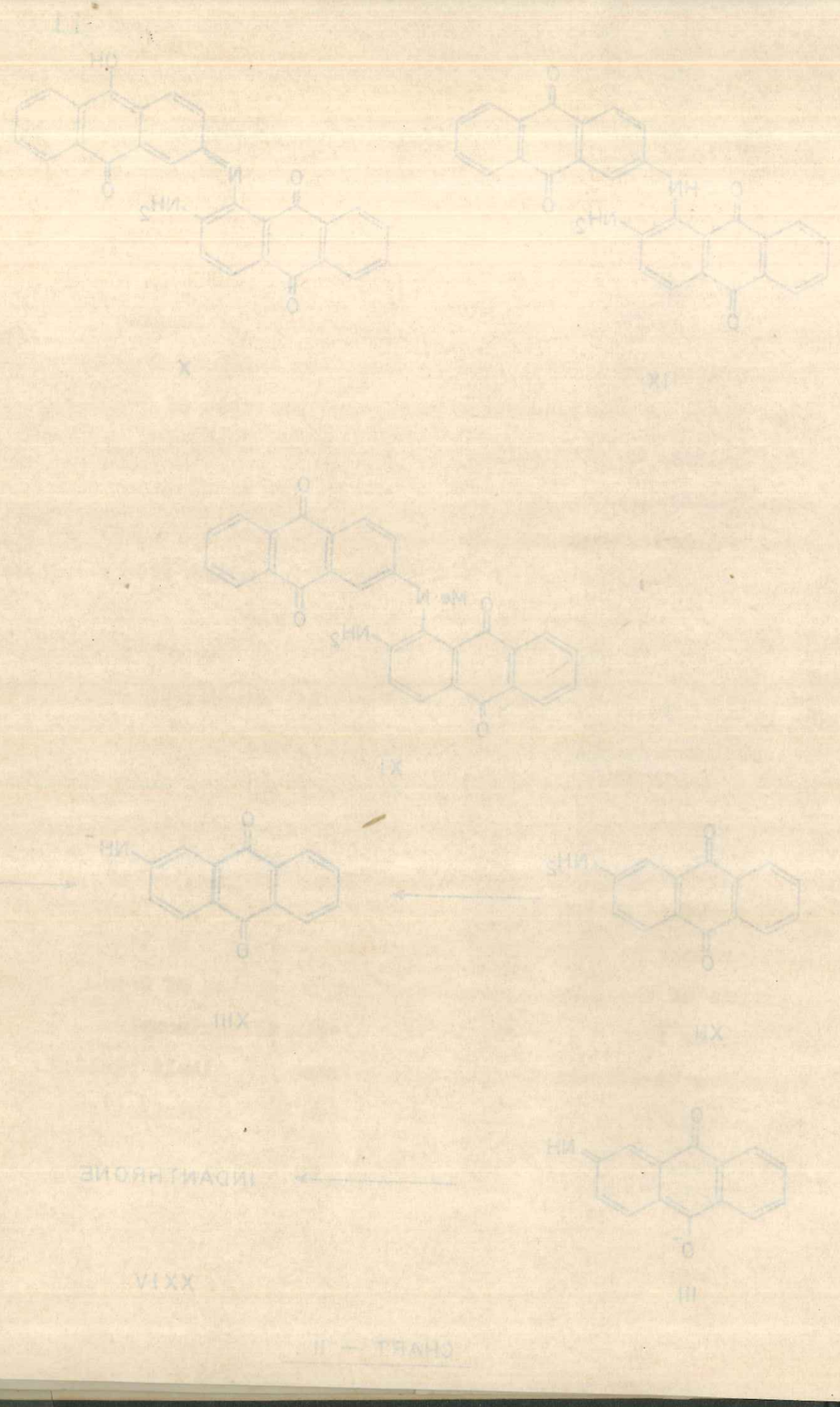


III

INDANTHRONE

XXIV

CHART — II .



Formation of alizarin

Bradley, Leete and Stephens explained the formation of alizarin as follows (10). At lower temperatures of alkali fusion alizarin is formed in appreciable amounts, e.g. at 180° it formed 13% of the product. In the process of forming indanthrone, the initial step by which the anion of 2-anthraquinonylamine links to the 1-position of another molecule of 2-aminoanthraquinone is reversible. The direct hydroxylation of 2-aminoanthraquinone which leads to alizarin through the 2-amino-1-hydroxyanthraquinone is, however, not a reversible process, and below 200° it represents an important side reaction. At higher temperatures the rate of substitution by hydroxyl and by 2-anthraquinonylamine anions increases and the formation of indanthrone is favoured because the end product is stable and the rate at which it is formed is higher.

The mode of formation of flavanthrone

The caustic potash fusion of 2-aminoanthraquinone at 300° mainly yields flavanthrone. Bohn's discovery of flavanthrone as a by product in indanthrone fusion was explained by Scholl as a result of the dehydrogenation of two molecules of 2-aminoanthraquinone to form 2 : 2'-diamino-1 : 1'-dianthraquinonyl. According to Schwenk 2-aminoanthraquinone and alkali yielded the radical (XIV) (probably XIV a) which on polymerisation gave flavanthrone (XV).

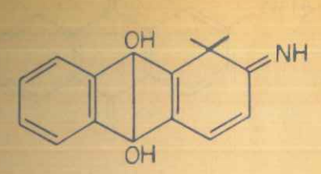
Bradley and Nursten (11) suggested that the formation of flavanthrone probably originated in the process of ionisation as in indanthrone, the anion reacting with the second molecule of 2-aminoanthraquinone in the form (XVI) (chart III).

The mechanism of formation of Indanthrene B (12)

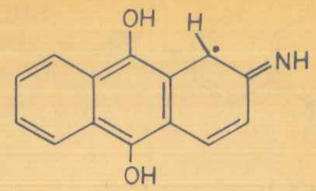
Both Maki and Tanaka have shown that when 2-aminoanthraquinone was heated with caustic potash at 150°, 2-amino-1-hydroxyanthraquinone (XVIII) was formed, which by further action of alkali was converted into alizarin (XIX). At the temperature at which the formation of indanthrene B, and also alizarin, is most probable viz. 150-200°, it is probable that both 2-amino-1-hydroxyanthraquinone and 1'-hydroxy-2-amino-1,2'-dianthraquinonylamine (XXI) are present in the alkali melt, formed by the hydroxylation of 2-aminoanthraquinone and 2-amino-1,2'-dianthraquinonylamine (IX) respectively (chart IV).

Of the two possible routes to the formation of the hydroxy compound (XXI), that through (IX) is favoured because the anion (XIII) from 2-aminoanthraquinone is a stronger nucleophilic reagent than the anion (XX) from 2-amino-1-hydroxyanthraquinone.

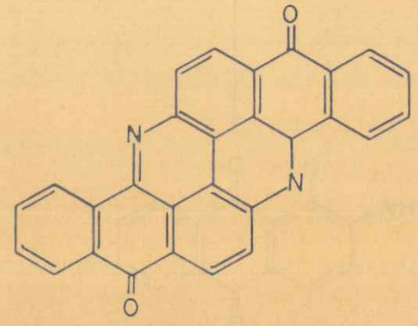
In the alkali fusion of 1-aminoanthraquinone, much higher yields of indanthrone are obtained and the formation of by products is found to be much less. It is much more difficult for hydroxylation to take place at the 2-position in 1-aminoanthraquinone than at the 1-position in 2-aminoanthraquinone, on account of the



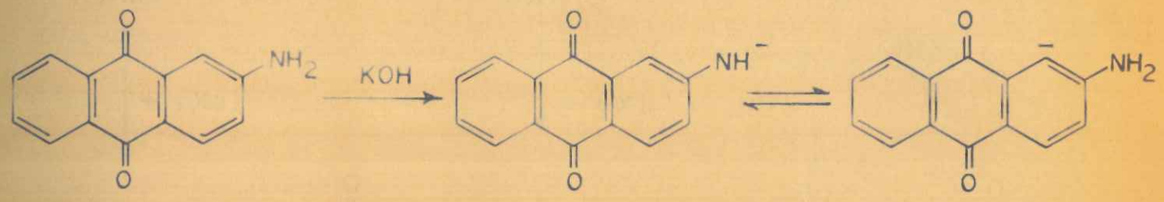
(XIV)



(XIVa)



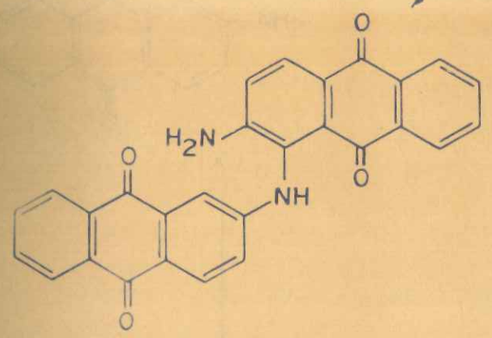
(XV)



(XII) (XIII) (XVI)

2-aminoanthraquinone

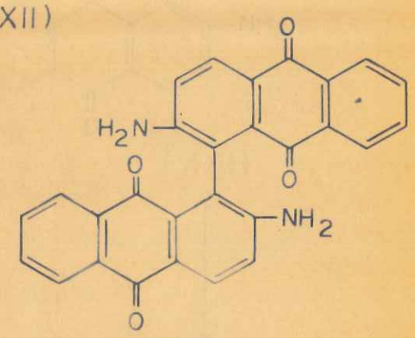
(XII)



(IX)

INDANTHRONE

(XXIV)



(XVII)

FLAVANTHRONE

(XV)

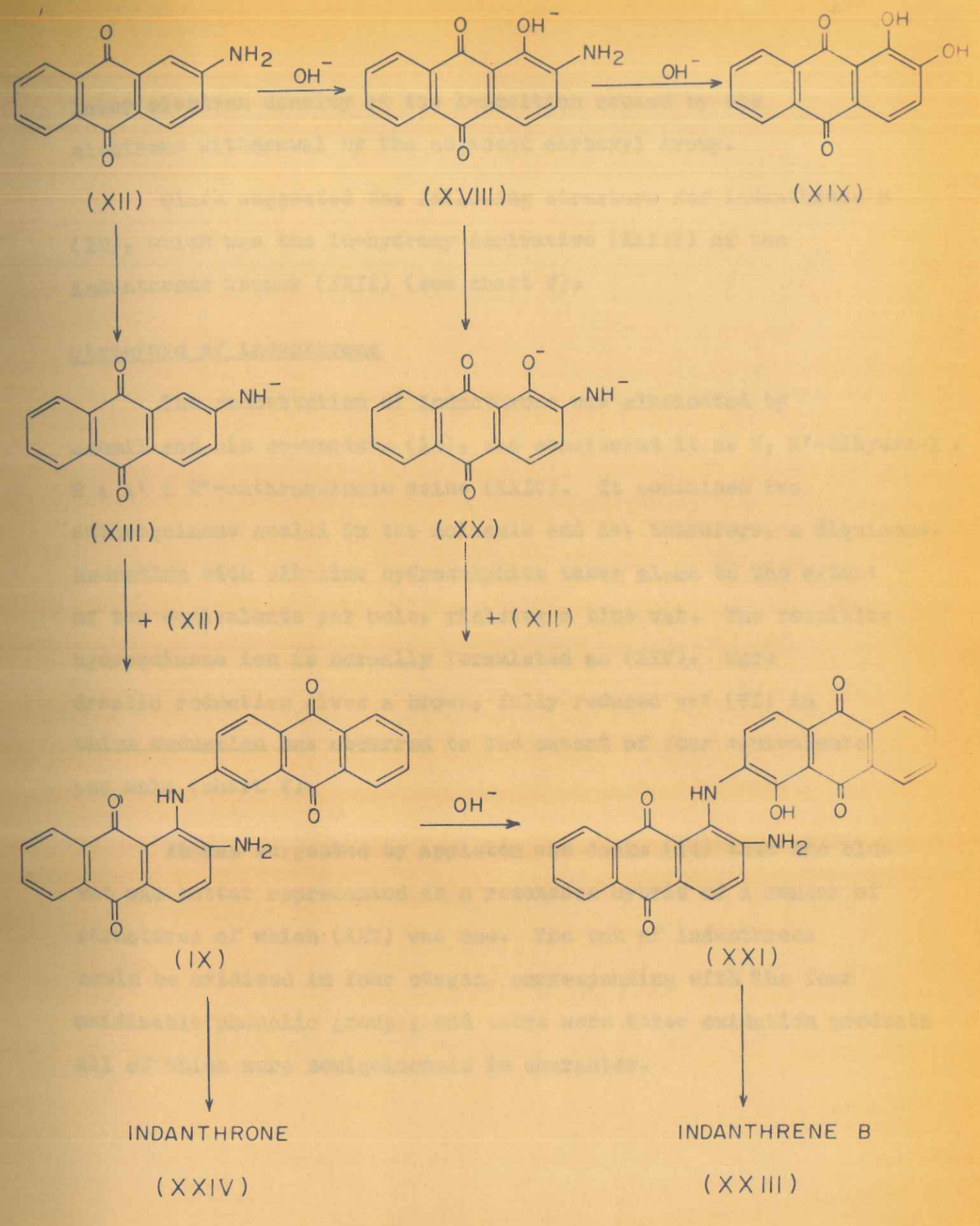

NH2
OH⁻
OH
(XII)
(XVIII)
(XIX)
NH⁻
O⁻
(XIII)
(XX)
+ (XII)
HN
(IX)
(XXI)
INDANTHRONE
(XXIV)
INDANTHRENE B
(XXIII)

CHART IV

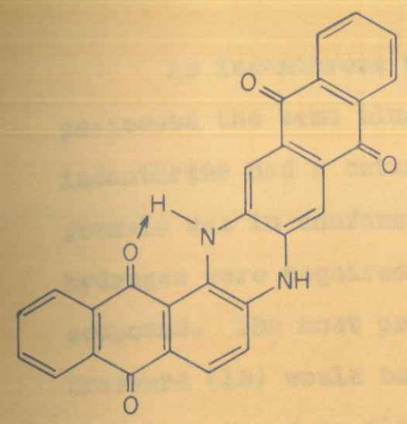
lower electron density at the 1-position caused by the electrons withdrawal by the adjacent carboxyl group.

Clark suggested the following structure for indanthrene B (12), which was the 16-hydroxy derivative (XXIII) of the indanthrone isomer (XXII) (see chart V).

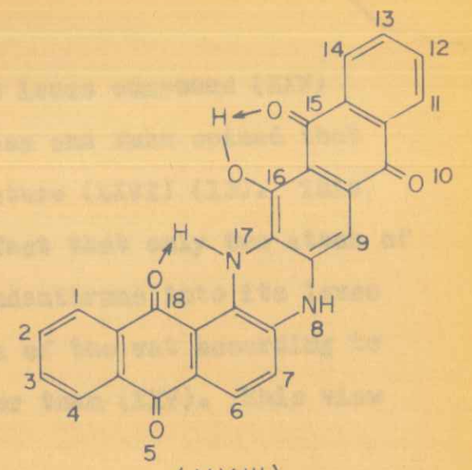
Structure of indanthrone

The constitution of indanthrone was elucidated by Scholl and his co-workers (13), who considered it as N, N'-dihydro-1 : 2 : 1' : 2'-anthraquinone azine (XXIV). It contained two anthraquinone nuclei in the molecule and is, therefore, a diquinone. Reduction with alkaline hydrosulphite takes place to the extent of two equivalents per mole, yielding a blue vat. The resulting hydroquinone ion is normally formulated as (XXV). More drastic reduction gives a brown, fully reduced vat (VI) in which reduction has occurred to the extent of four equivalents per mole (chart V).

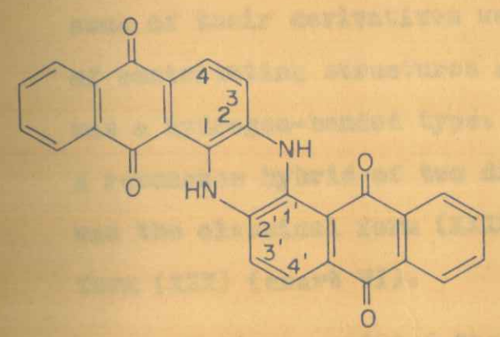
It was suggested by Appleton and Geake (14) that the blue vat was better represented as a resonance hybrid of a number of structures of which (XXV) was one. The vat of indanthrone could be oxidised in four stages, corresponding with the four oxidisable phenolic groups, and there were three oxidation products all of which were semiquinonoid in character.



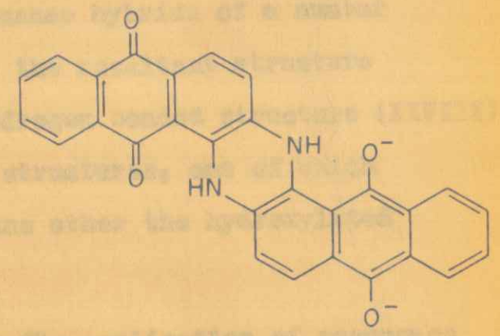
(XXII)



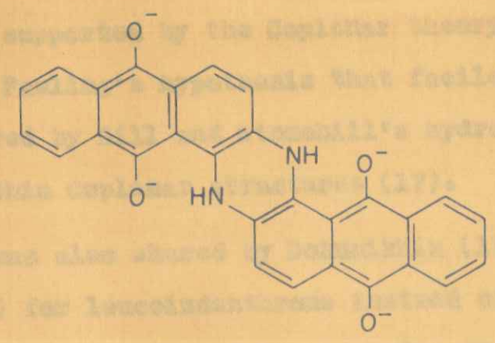
(XXIII)



(XXIV)



(XXV)



(VI)

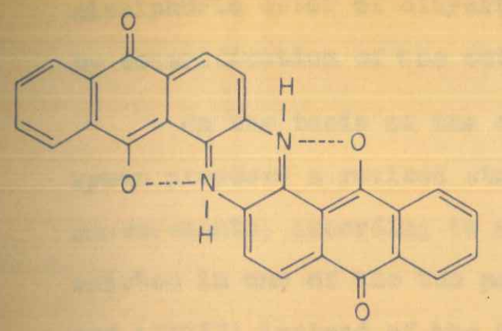
CHART - V

As indanthrone (XXIV) and its leuco compound (XXV) possessed the same blue colour, claasz and Kuhn opined that indanthrone had a betaine-like structure (XXVI) (13). This formula was in conformity with the fact that only two atoms of hydrogen were required to convert indanthrone into its leuco compound. The most probable formula of the vat according to Brassard (13) would be (XXVII) rather than (XXV). This view was also shared by Clibbens (15).

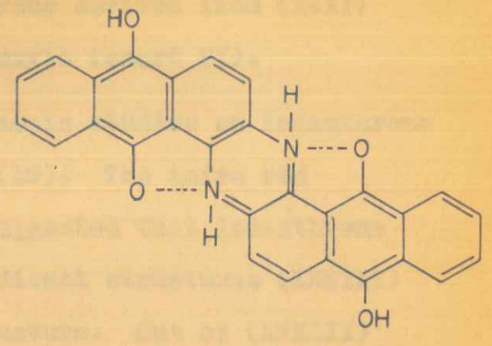
According to Gill and Stonehill (16) indanthrone and some of their derivatives were resonance hybrids of a number of contributing structures and that the resultant structure was a hydrogen-bonded type. The hydrogen bonded structure (XXVIII) was a resonance hybrid of two distinct structures, one of which was the classical form (XXIX) and the other the hydroxylated form (XXX) (chart VI).

Robinson pointed the way for the application of resonance theory to indanthrone structure (17). The conclusion of Gill and Stonehill was supported by the Coplanar theory of substantive dyes, and also by Pauling's hypothesis that facile resonance, such as was required by Gill and Stonehill's hydrogen bond theory, can only occur within Coplanar structures (17).

This view was also shared by Dokunikhin (18) who suggested the formula (XXXI) for leucoindanthrone instead of Scholl's formula (XXV). This was confirmed by preparing the red disulphuric ester (XXXII) which was found to be quite distinct from the violet



(XXVI)



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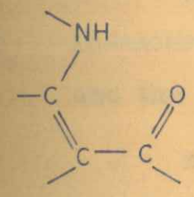

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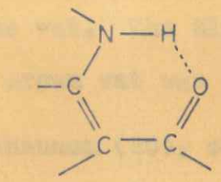
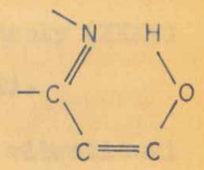


(XXVIII)



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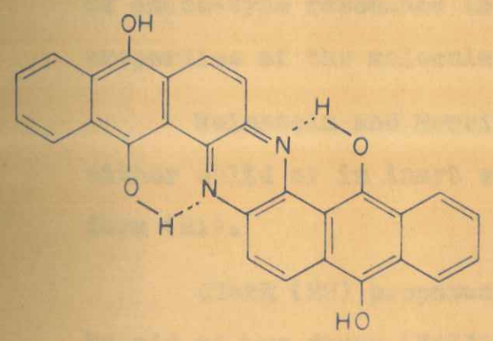

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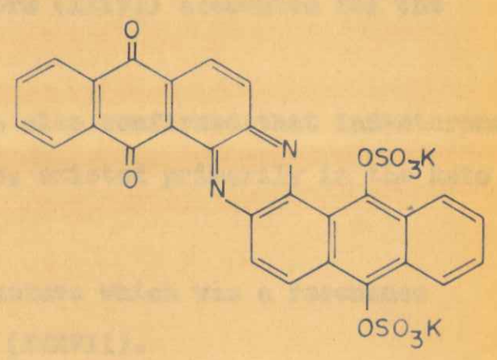


(XXXII)

CHART — VI

disulphuric ester of dihydroindanthrone derived from (XXXI) by esterification of the outer hydroxyls (chart VI).

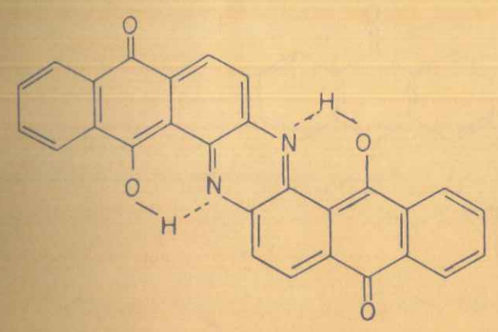
On the basis of the spectroscopic studies on indanthrone Wyman proposed a revised structure (19). The infra red measurements, according to Wyman, suggested that indanthrone existed in one of the two possible dienol structures (XXXIII) and (XXXIV) instead of the keto structure. Out of (XXXIII) and (XXXIV) Wyman preferred (XXXIII).

This structure readily explained the reduction of indanthrone to the blue vat. The blue vat was probably (XXXV) and the fully reduced brown vat was (VI) (chart VII).

But Durie and Shannon (20), on the basis of vibrational and electronic absorption spectra of indanthrone and other available evidence favoured the conventional tetraketo form rather than the enol form proposed by Wyman. The postulation of amide-type resonance in the form (XXXVI) accounted for the properties of the molecule.

Weinstein and Merritt, Jr. also confirmed that indanthrone, either solid or in inert solvents, existed primarily in the keto form (21).

Clark (22) proposed a structure which was a resonance hybrid of two forms (XXXIII) and (XXXVII).



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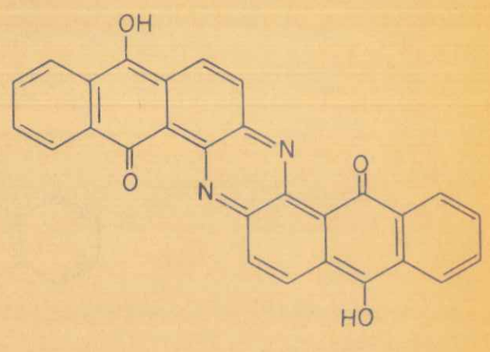

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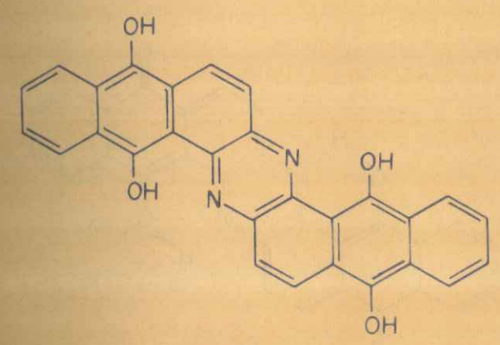

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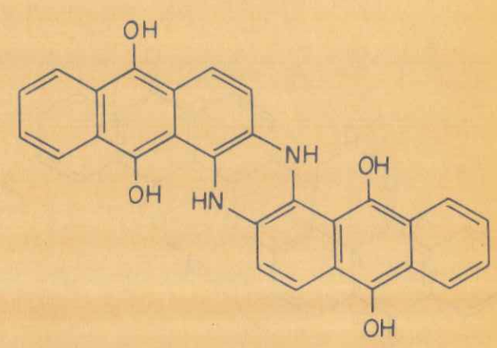
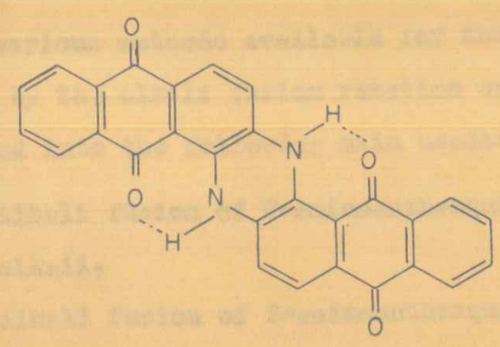
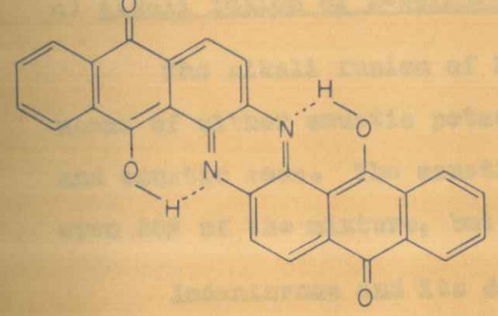


(VI)

CHART – VII.



(XXXVI)



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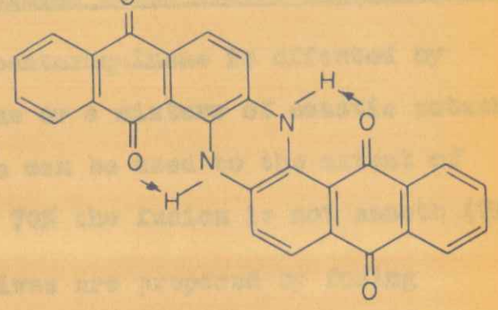
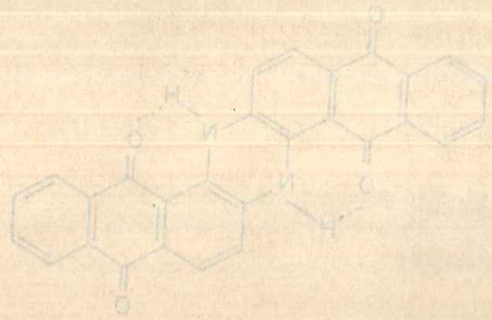


(XXXVII)

CHART – VIII



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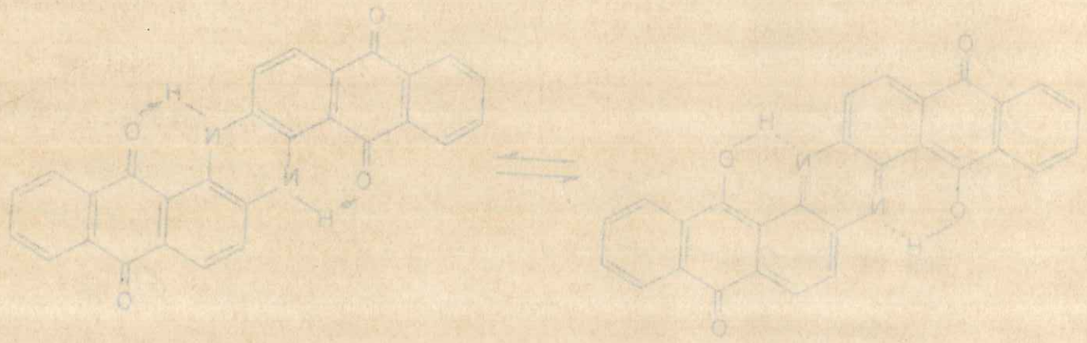


(IIIVXXX)

(IIIXXX)

Technology of indanthrone preparation

The various methods available for the preparation of indanthrone by the alkali fusion reaction or otherwise can be classified into the following main heads:

(a) Alkali fusion of 2-aminoanthraquinone in molten caustic alkali,

(b) Alkali fusion of 2-aminoanthraquinone in presence of a diluent,

(c) Alkali fusion of 2-aminoanthraquinone by a continuous process,

(d) Alkali fusion of 1-aminoanthraquinone to indanthrone, and

(e) Alkaline ring closure of 1-aminoanthraquinone and 2-aminoanthraquinone using suitable solvent and other methods

a) Alkali fusion of 2-aminoanthraquinone using molten caustic alkali

The alkali fusion of 2-aminoanthraquinone is effected by means of either caustic potash alone or a mixture of caustic potash and caustic soda. The caustic soda can be used to the extent of even 50% of the mixture, but above 70% the fusion is not smooth (23).

Indanthrone and its derivatives are prepared by fusing 2-aminoanthraquinone or its derivatives in the presence of salts of lower as well as higher fatty acids, e.g., potassium formate, tartrate, acetate, or sodium acetate and valerate. An oxidising agent such as potassium chlorate may be added. An alcoholate like sodium methylate, ethylate, butylate, isoamylate, diethylene glycolate or glycerate and also phenolic compounds such as sodium phenolate, cresolate, resorcinate or naphtholate, or a plurality of the alcoholates or phenolates increase the yield of the dye (24-35).

According to Maki addition of phenols and naphthols accelerated the formation of indanthrone over alizarin. When the alkali fusion was carried out using phenol at 180° for 1 hour, it gave an yield of 51.5% of indanthrone (36). The fusion without phenol gave only 18% of the dye. A certain quantity of phenol acted as catalyst while the excess was diluent. The catalytic action of the cresol isomers was not uniform, the meta isomer having a lesser effect (3). It was also found that phenols and other hydroxy derivatives raised the yield of indanthrone but did not affect the formation of by products, indanthrene B and C which amounted to about 20% yield irrespective of the additions (34).

Fusion of 2-aminoanthraquinone with caustic potash and a sugar, such as glucose, cane sugar, or lactose gives indanthrone (37). It is also fused with caustic alkali at 220-40° in presence of an inorganic salt or salts capable of acting as reducing agents (38,39). Improved yields are reported in such cases. The inorganic salts mentioned are cyanides, sulphides, and ferrocyanides of the alkali metals.

2-aminoanthraquinone is fused with alkali in the presence of hydroxy aliphatic secondary or tertiary amines, e.g., di- or triethanolamine at 200° along with other known ingredients (40).

Boric acid, its simple or complex salts, or a mixture of them are used in the fusion of 2-aminoanthraquinone (41). The addition of soyabean protein (42, 43) to the fused alkali accelerated the reaction and increased the yield. The reason for the increased

yield was due to the improved wetting property of the raw material in the alkali melt and consequent prevention of its sublimation. It was also confirmed that the leucine present in soyabean played an important role.

A mixture of caustic potash (34 parts), water (6 parts), and alkaline lignin (4 parts) was heated at 200-20° for 20 minutes, and continued heating for 20 minutes more with 2-aminoanthraquinone (10 parts) at the same temperature, cooled, diluted, aerated, and the dye refined by use of sodium hydrosulphite to give indanthrone (4.5 parts) (44).

2-aminoanthraquinone on being reacted with caustic alkali, was added in the form of an aqueous slurry to facilitate smooth reaction (45).

A mixture of 2-aminoanthraquinone and caustic potash is ground in a mill together and then passed in a thin layer through a heated chamber to obtain indanthrone (46). The fusion is also carried out in a rotation oven equipped with crushing balls. The resulting melt is processed further after dissolution in the same or another equipment (47).

In the German process (48) for indanthrone, an alkali melt consisting of potassium hydroxide (670 parts), sodium hydroxide (270 parts) and water (3-4 parts) and anhydrous sodium acetate (220 parts) was reacted, under nitrogen atmosphere, with 2-aminoanthraquinone (500 parts; 86-87% purity). The 2-amino-anthraquinone was fed at 180° by means of a screw conveyor over a period of 20 minutes. A mixture consisting of sodium

nitrate (60 parts), caustic potash (40 parts) and caustic soda (20 parts) was then added in the course of 2-3 hours. The temperature of the melt was kept at 200-25°. The product was drawn into water (11000 parts) and the reaction kettle was rinsed out with another 2000 parts of water. The dye was vatted at 45-8° for 2 hours with sodium hydrosulphite (750 parts of 15% solution). The leuco crystals were filtered off at 25-30° until the filtrate ran pale green. The filter cake was stirred with water (1000 parts) and caustic soda (50%, 20 parts) and oxidised at 60° by air. The dye was filtered and stirred with water (2000 parts) and sulphuric acid (96% 80 parts) at 60°, followed by filtration, washing neutral and drying. The yield of indanthrone was 56.5% (by weight).

The effect of variation in the temperature of the fusion was studied by Maki (36). Fusion at 180° for 1 hour gave the maximum yield of 51.5%. At 210° the reaction was completed in 15 minutes. The decomposition velocity was unduly increased beyond 210°.

The studies by Maki (49) on the decomposition of indanthrone in alkali melt have indicated that when finely powdered indanthrone (5 parts) was heated with potassium hydroxide (75%, 30 parts) at 250°, there was 36% decomposition after 15 minutes and 48% after 30 minutes. The reaction curve rose about as the third power giving an average velocity constant equivalent to 0.047. At 150°, the decomposition was 8% in 1 hour, at 180° it was 16%, at 200° it was 25%, at 250° it amounted to 61% and at 290° it was very considerable, i.e. 85%.

b) Alkali fusion in presence of a diluent or solvent

A highly reactive alkaline reagent is a mixture of caustic potash with ethanol or methanol in quantity not exceeding half a mole proportion while avoiding pressure or admission of air as far as possible. This reagent could be substituted for molten caustic alkali for fusion reactions. The reaction is carried out by mixing 2-aminoanthraquinone with caustic potash and ethanol, while avoiding air introduction, and then spreading the mixture in thin layers in air. Or a mixture of caustic potash and 2-aminoanthraquinone is spread out in the air and the required quantity of alcohol sprayed over it. The process may be carried out in a continuous manner and the evaporated alcohol recovered (50).

The alkali fusion is effected in presence of an indifferent solvent or diluent (51-53). Less alkali is employed than usual by use of the solvent. The solvent should boil at or above the reaction temperature, say about 230°. A purified kerosene oil is preferred. The dye is obtained in a finely divided form. In a typical process, caustic potash (30 kg) is gradually added to a mixture of mineral oil (200 l.) and 2-aminoanthraquinone (40 kg) at about 220-5° and the temperature is then raised to about 230° for completion of the reaction and evolution of water vapour.

c) Continuous process for indanthrone from 2-aminoanthraquinone (54)

With a view to reduce the occurrence of local overheating and the side phenomena associated with it and also the foaming of the melt, Yoshio Nagai fabricated a device consisting of an externally

heated groove-formed boat with a stirring shaft, running in the longitudinal direction. The stirring pads were so built that at the delivery end for the reactants there was a strong mixing and in the remaining portion there was a low mixing till the exit opening. In order to make the device adaptable to various properties accompanying the raw materials easily, the stirrer r.p.m. was made adjustible over a wide range (200-2500), and the angular position of the stirrer pads to the axis of the stirrer shaft.

2-aminoanthraquinone (30 parts) was charged with an alkali fluxing material (80 parts) consisting of caustic potash (68 parts), caustic soda (27 parts) and sodium acetate (22 parts) through the delivery end. The stirrer r.p.m. was adjusted to 1850 and the reaction temperature was maintained constantly at 220° from the delivery to the outlet point. The yield of indanthrone obtained was 65.9% (by weight) and the dye was of commercial strength.

d) <u>Alkali fusion of 1-aminoanthraquinone to indanthrone</u>

An improved process for preparing indanthrone from 1-amino-anthraquinone is described (55-57). Potassium hydroxide (90%, 100 parts) was added to molten phenol (150 parts) at 100-20°; the resultant potassium phenolate was mixed with anhydrous sodium acetate (40 parts) at 160-80°. Sodium formate, propionate or butylate could also be used in place of the acetate. A mixture of 1-aminoanthraquinone (100 parts) and sodium chlorate (5-20 parts) was added in lots during 30-60 minutes. Ferric oxide or manganese dioxide (1 part) was then added and the melt heated to 200° and stirred for 2.5 - 7 hours while the temperature was gradually increased to 210°. The

melt was taken in water (3000 parts) and heated to boiling for 1 hour, the resultant crude dye was filtered, washed, dried and then purified from sulphuric acid (83%) to give indanthrone, 68.2 parts, i.e. 70% yield. The acid filtrate was further diluted and the product was sublimed to give recovered 1-aminoanthraquinone (9.6 parts).

The above process has been modified as under (58). Indanthrone was prepared from 1-aminoanthraquinone by oxidation with oxygen containing gases, like air, in the presence of oxidation catalysts. Thus potassium hydroxide (90%, 50 parts) were reacted with molten phenol (75 parts) at 100°, and then it was heated to 130°. Sodium acetate (20 parts) was added at 140-60°, followed by manganous sulphate (1.5 parts) and copper acetate (2 parts), and then 1-aminoanthraquinone (5 parts) at 195-200° with vigorous stirring along with introduction of air, the temperature being maintained at 210° for 3 1/2 hours and then at 220° for 2 1/2 hours more. The melt was taken in water (2 l) and boiled for 1 hour. A concentrated solution of sodium bisulphite (5 ml.) was added and the mixture was filtered hot, the filter cake was washed with hot water and dried. The dye was subsequently purified from 83% sulphuric acid.

e) <u>Alkaline ring-closure of 1- and 2-aminoanthraquinones using suitable solvents and other methods</u>

Alkaline ring closures to produce vat dyes like indanthrone were accomplished without an alkali fusion by conducting the reaction in a rotatable ball - or rod - mill at high temperatures (59).

A mixture of dimethyl sulphoxide (90 parts), aqueous potassium hydroxide (50%, 240 parts), and 1-aminoanthraquinone (10 parts) were refluxed under stirring at 115-20° for 7 hours, diluted with alcohol, filtered, washed with alcohol, and dried to give indanthrone. The addition of suitable ingredients, like sodium borate, vanadium pentoxide and others to dimethyl sulphoxide are also mentioned (60).

Methods of purification of indanthrone

Indanthrone is purified (61) from admixed flavanthrone by treating the crude reaction product with alkali or alkali earth hypochlorites like sodium hypochlorite, chlorates, permanganates, or persulphates, and subsequently filtering and washing.

Indanthrone is also purified by dissolving the fusion product in water and the alkali metal salt of the leuco dye is crystallised from the resulting solution (62).

Pure indanthrone is prepared by precipitating the sulphate from its solution in sulphuric acid of high percentage, followed by addition of dilute sulphuric acid and hydrolysing the sulphate with water. It is then filtered and washed (63).

Miscellaneous methods of preparation

Indanthrone is obtained by dehalogenating halo indanthrones such as dibromoindanthrone formed by condensing 1,3-dibromo-2-amino-anthraquinone. The dehalogenation is caused by alcoholic potash, sodium amalgam, glucose and caustic alkali, and copper with or without a diluting agent or catalyst (64, 65).

Indanthrone or its chloro derivatives are produced by condensation of either 1-chloro-2-aminoanthraquinone or 1,3-dichloro-2-aminoanthraquinone in the presence of a copper catalyst such as cuprous iodide and an inert liquid reaction medium such as molten naphthalene or orthodichlorobenzene and an acid-binding medium such as anhydrous sodium acetate or sodium carbonate. Similar condensations are also carried out using cuprous bromide in place of the iodide. The cuprous halide is prepared by direct union of finely divided copper and a halogen in an organic solvent (66-70).

Indanthrone disulphonic acid is desulphonated by electrolytic reduction in a divided cell, in alkaline solution (71).

2-aminoanthrahydroquinone-9,10-disulphuric ester is oxidised by using cupric sulphate or chloride with the addition of sodium hydroxide or hydrochloric acid in order to prevent over-oxidation and obtain indanthrone (72). The disulphuric ester of 2-aminoanthraquinone is prepared by treating the amine with sulphur trioxide compounds of strongly basic tertiary amines in aqueous medium. The oxidation of the disulphurid ester is also done in the same medium with hypochlorites, ferric chloride and hydrochloric acid, ferricyanides, silver salts, etc. (73).

The tetrasulphuric ester of leuco indanthrone is also formed when the alkaline solution of 2-aminoanthrahydroquinone disulphuric ester is heated with lead superoxide (74). The yield of indanthrone is reported to be 68%.

Heating 5 g of 1,2-anthraquinone, 100 ml. of formamide and 5 ml of acetic acid at 150° gives bis-ang-dianthraceno-pyrazine (anthrazine). Oxidation with dichromate in sulphuric acid gives

indanthrone (75).

2,9,10-triaminoanthracene (22.3 g) is boiled with 10 volumes of pyridine followed by addition of potassium permanganate (10.5 g) and keeping for 15 minutes after which pyridine (10 volumes) is again added; the product is filtered hot and the solution evaporated to give indanthrone in 50% yield. By starting from 2-aminoanthracene-9,10-bis (pyridinium chloride), indanthrone is obtained in a similar fashion in 46% yield (76).

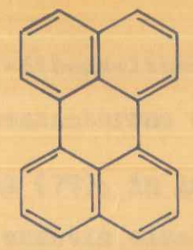
Chemistry of dibenzanthrone

Dibenzanthrone, one of the oldest known anthraquinone vat dyes, is a polycyclic quinone containing a perylene nucleus which is made up of nine condensed benzene rings and two keto groups (77). It was discovered by Oskar Bally in the year 1905, when he applied the technique of the action of fused alkali hydroxides for deciding the structures of benzanthrone - quinoline and benzanthrone (78).

The constitution of the new dye was established by Scholl who showed that naphthalene, on heating with aluminium chloride, yielded perylene (XXXVIII), and that phenyl α-naphthyl ketone with the same reagent gave benzanthrone. He synthesised dibenzanthrone (XL) from dibenzoyldinaphthyl (XXXIX) (78).

As in indanthrone, the name of the dye, violanthrene was subsequently changed to violanthrone or dibenzanthrone in recognition of its ketonic nature (78).

Bally's preparatory method for dibenzanthrone was to fuse two molecules of benzanthrone through a common benzene ring. The benzanthrone nuclei are joined either as 3,3'-dibenzanthronyl



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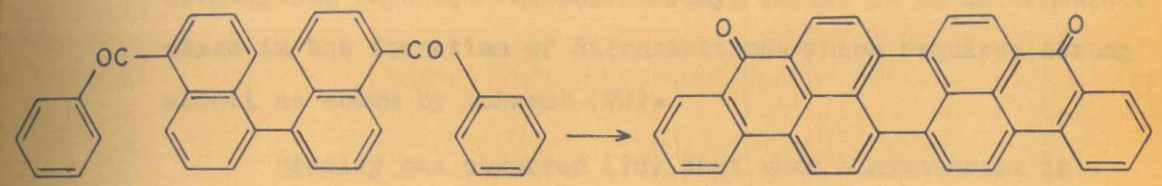
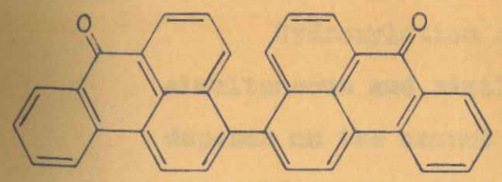
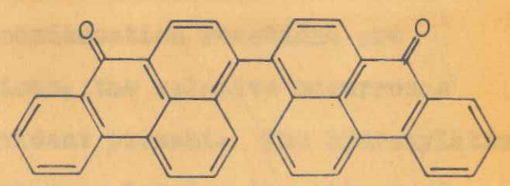


(XXXIX) (XL)





(XLI) (XLII)

CHART – IX

(XLI) or 4,4'-dibenzalthronyl (XLII) which are further ring closed to dibenzanthrone (XL) (77).

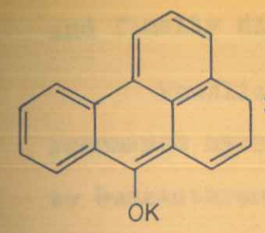
Schwenk (78), in 1923, put forward that benzanthrone reacted with caustic alkali to give the diradical (XLIII) which formed dihydrodibenzanthronyl (XLIV) on polymerisation and subsequently dibenzanthrone (XL).

Luttringhaus and Neresheimer, in the next year also established that 4,4'-dibenzanthronyl (XLII) is an intermediate stage in the formation of dibenzanthrone which required strong alkali as shown by Schwenk (79).

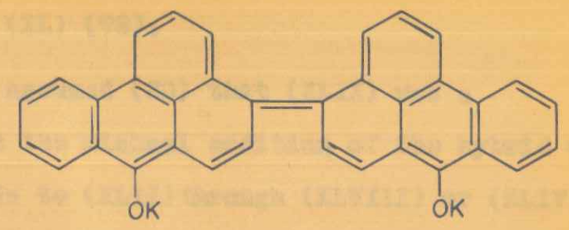
Bradley has observed (78) that when benzanthrone is heated with caustic potash, the result is greatly influenced by the presence or absence of oxidants. The product is mainly hydroxy benzanthrone (XLV) in the presence of an oxidant, but when it is less, the formation of dibenzanthronyl and dibenzanthrone is favoured. In the absence of oxidants, self-condensation becomes the main reaction.

Hydroxylation and self-condensation reactions are simultaneous and similar reactions, the relative occurrence depends on the amount of the oxidant present. The hydroxylation and self-condensation of benzanthrone involve the attack of anions (hydroxyl and the anion of benzanthrone) on benzanthrone.

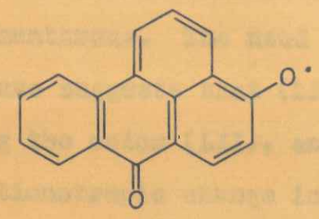
For the formation of dibenzanthronyl having the structure postulated by Luttringhaus and Neresheimer, the benzanthrone anion should have the structure (XLVII). The anion of benzanthrone will attack unionised benzanthrone to form the adduct (XLVIII) which is changed to dibenzanthronyl,



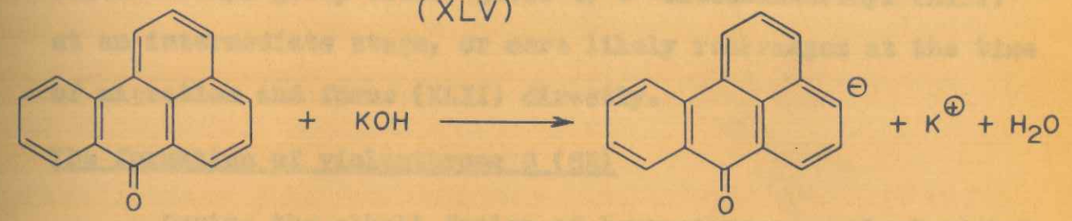
(XLIII)



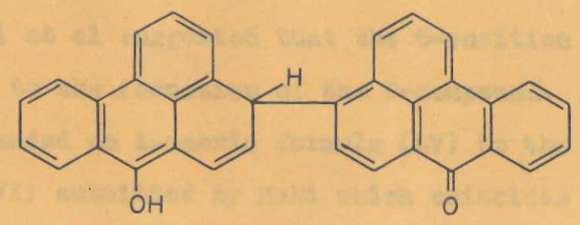
(XLIV)



(XLV)



(XLVI) (XLVII)



(XLVIII)

CHART – X .

and finally dibenzanthrone (XL) (78).

Wanzlick and Ahrens assumed (80) that (XLIX) was a resonance hybrid of (L) and the michael addition of the hybrid (L) to benzanthrone (XLVI) leads to (XLII) through (XLVIII) or (XLIV).

Bradley and Jadhav (81) found that 6, 6'-dibenzanthronyl (LI) reacts with potassium hydroxide at 240-50° to form a mixture of acids together with some dibenzanthrone. The main product at 260-70° was dibenzanthrone. The need of a strong alkali and elevated temperature suggests that (LI), like (XLVI) is a very weak acid yielding the anion (LII), and that (XLII) is formed from this by a cationotropic change in which the migrating benzanthronyl group either gives 4, 6'-dibenzanthronyl (LIII) at an intermediate stage, or more likely rearranges at the time of migration and forms (XLII) directly.

The formation of violanthrone B (82)

During the alkali fusion of benzanthrone, a black violet by-product which is worthless as a vat dye is obtained. Maki named it violanthrone B and suggested the formula (LIV) with one carbonyl group.

Nagai et al suggested that the 6-position of benzanthrone contributes to the formation of the B-compound. Consequently, Aoki recommended an isomeric formula (LV) to the hypothetic skeleton (LVI) submitted by Maki which coincides with the above facts.

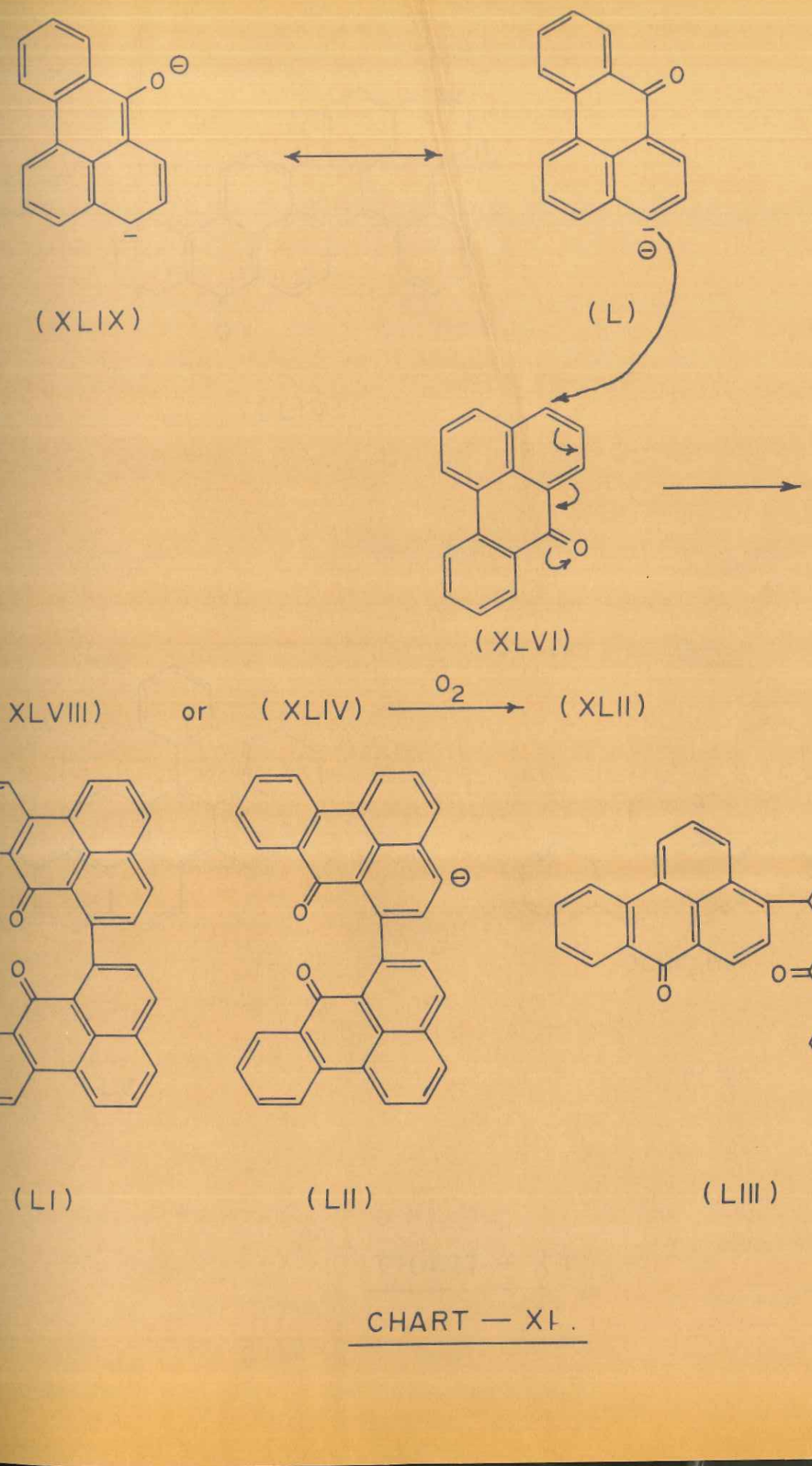
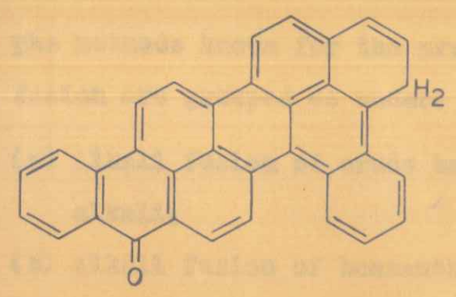
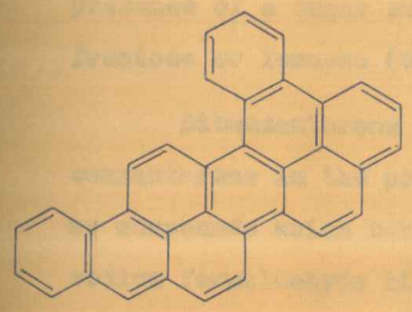


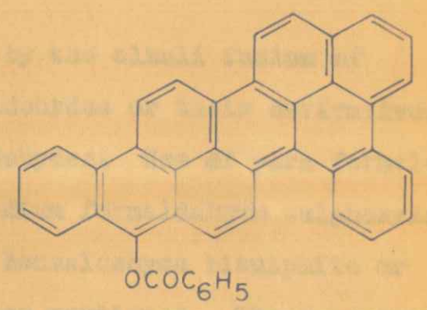
CHART — XI.



(LIV)

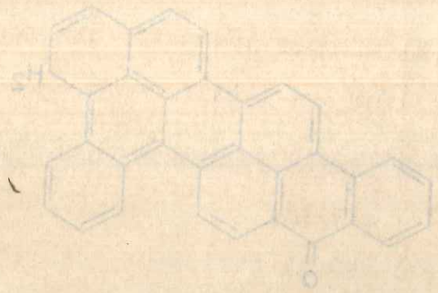


(LV)



(LVI)

CHART – XII



Technology of dibenzanthrone preparation

The methods known for the preparation of dibenzanthrone by alkali fusion are grouped as under:

(a) Alkali fusion of crude benzanthrone using molten caustic alkali,

(b) Alkali fusion of benzanthrone in presence of a solvent,

(c) Cyclisation of 3,3'-and 4,4'-dibenzanthronyls to dibenzanthrone, and

(d) Miscellaneous methods

(a) Alkali fusion of benzanthrone using caustic alkali melt

Benzanthrone is fused with caustic potash in the presence of a sugar such as glucose, cane sugar, lactose, fructose or formose (83, 84).

Dibenzanthrone is prepared by the alkali fusion of benzanthrone in the presence of aldehydes or their derivatives or compounds which behave like aldehydes. Use of para formaldehyde, sodium formaldehyde bisulphite, sodium formaldehyde sulphoxylate, sodium glyoxal bisulphite, sodium benzaldehyde bisulphite or the corresponding zinc compounds are mentioned. The amount of the aldehyde derivatives used is 15-20% of the weight of benzanthrone (85-87).

A mixture of benzanthrone, caustic potash (81%) and phenol in the ratio of 5 : 20 : 6.2 at a temperature of 220° gives 49.2% yield of dibenzanthrone. Increase in the quantity of phenol and conducting the reaction at lower temperatures increased the yield of the dye (88-90).

Benzanthrone, caustic potash and finely divided aluminium are heated together at 235-40° to get dibenzanthrone (91).

The presence of alkali-insoluble impurities in benzanthrone during the alkali fusion along with a reducing agent is reported to increase the yield of the dye (92).

Oxidising agents, e.g. metal peroxides, chromates, bichromates and permanganates of alkali metals, metal nitrates and chlorates, oxides and salts of copper and nitrobenzene sulphonic acids are used in the alkali fusion of benzanthrone to get very high yields of dibenzanthrone. An acetate or propionate of an alkali metal may be added to inhibit the formation of other undesirable products like isodibenzanthrone. Oxidising agents, such as sodium nitrite or chlorate are also added to the melt before processing the dye in order to get a product free from impurities (93-95).

Boric acid, its simple or complex salts, or a mixture of them is used in the alkali fusion of benzanthrone with potassium hydroxide to form dibenzanthrone (96).

A mixture of benzanthrone (10 parts), phenanthrene (25 parts), sodium hydroxide (13 parts) and potassium hydroxide (19 parts) heated first at 180° and then at 225°, and the reaction product suitably purified, gave dibenzanthrone (6 parts). When anthracene was used instead of phenanthrene, the yield was somewhat lower, which was further reduced (50%) when neither of them was used (97).

Benzanthrone is alkali fused with potassium hydroxide along with sodium acetate and sodium nitrate in the presence of diphenyl or 2-(or 4-)hydroxydiphenyl to give dibenzanthrone with nearly 85% yield (98).

In the I.G. process (99), benzanthrone (240 parts) and 'anthracene residues poor in carbazole' or naphthalene as flux are melted together at 120°, and a mixture consisting of 67-68% caustic potash and 27-28% caustic soda (600 parts) as in the case of indanthrone fusion, along with anhydrous sodium acetate (50 parts) is added. The reaction commences at 180° and is carried out at 225-30° for 1 to 1.5 hours. The dye is purified by vatting, clarifying the solution with Kieselguhr, filtering, and reoxidising. The yield of the dye is about 78.7%.

(b) <u>Alkali fusion of benzanthrone in presence of a solvent</u>

Alkali fusion of benzanthrone is effected using liquid hydrocarbons such as kerosene having a boiling point of about 230°. Less alkali than usually needed is employed in such processes. A reducing agent like dextrin, starch, cellulose, aminophenols, and others is also added (100-103).

Benzanthrone is heated with alcoholic potash at 140° or in a naphthalene melt in presence of oxidising agents such as air, and with the addition of an oxide of an alkali metal, e.g. sodium oxide, in an amount at least sufficient to take up the water in the reaction mass (104).

The fusion in presence of an oxidising agent is improved by carrying out the reaction in a cellosolve type of solvent, thus permitting the temperature of the reaction to decrease from 210° to

145° (105).

Benzanthrone, on fusion with an alkali mixture (potassium hydroxide : sodium hydroxide : : 14 : 10) in the presence of sodium nitrite and any ethanolamine or glycol (e.g. triethanolamine or triethylene glycol) under reduced pressure (500-600 mm.) at 160-70° for 1 hour, gives dibenzanthrone in 94-97% yield (106).

(c) Cyclisation of the dibenzanthronyls to dibenzanthrone

Cyclisation of 3, 3'-dibenzanthronyl

3, 3'-dibenzanthronyl is treated with alcoholic caustic potash at 130° in presence of an indifferent solvent or diluent such as ketosene, xylene or petrol. Heating 10 parts of it with 50 parts of caustic potash and 50 ml. of methanol at 115-20° for 2 hours gives dibenzanthrone (108). The 3, 3'-dibenzanthronyl is converted to dibenzanthrone under much milder conditions of alkali fusion than the 4, 4'-derivative. It was also found that the cyclisation of the 3, 3'-derivative is facilitated by the presence of about a fifth of its weight of glucose (109). 107

The cyclisation of 3, 3'-dibenzanthronyl is also effected by heating in presence of the tetrachlorides or bromides of titanium or zirconium, forming thereby the titanium or zirconium complexes. After hydrolysis the dye, which is obtained in the reduced state, is subsequently oxidised to the quinone (110).

When 3,3'-dibenzanthronyl (17.5 parts) is refluxed with sodium hydroxide solution (3%; 1000 ml.) for one hour, the mixture filtered and the residue washed with a solution of sodium hydroxide and water, dibenzanthrone is obtained. When 10 parts of it are heated at 430° for 15 minutes and the residue washed with boiling chlorobenzene (200 parts), it gives 9.6 parts of dibenzanthrone. Similarly, when 10 parts of it is heated under a stream of nitrogen at 380-90° at 10 mm. pressure for 5 minutes and washed with chlorobenzene, 9.8 parts of dibenzanthrone are obtained (111).

3,3'-dibenzanthronyl, on treatment with sulphuric acid (85%) and arsenic acid (H_3AsO_4), gives dibenzanthrone by cyclisation (112).

Cyclisation of 4,4'-dibenzanthronyl

The ring closure of 4,4'-dibenzanthronyl is effected by using 80-90% sulphuric acid at 115-40° along with oxidising agents such as sodium nitrite, nitrosyl sulphuric acid, sodium arsenate and arseneous oxide (113).

Dibenzanthrone is obtained by oxidation of 4,4'-dibenzanthronyl in an 80-100% aqueous solution of hydrogen fluoride (114). In an example, 4,4'-dibenzanthronyl (1 part) was taken in hydrofluoric acid (97%; 5 parts), and potassium dichromate (1 part) being added portionwise at 10°. The

hydrofluoric acid was separated by distillation subsequently.

The thermal treatment of 4,4'-dibenzanthronyl as the 3,3'-compound yields dibenzanthrone (115). The 4,4'-derivative is also cyclised using aluminium chloride or caustic potash at 200-20° (116).

(d) Miscellaneous methods

Dibenzanthrone is obtained by baking dibenzoyl perylene with aluminium chloride (117).

4,4'-dibenzoyl-1,1'-binaphthyl, obtained from 1,1'-binaphthyl, benzoyl chloride and aluminium chloride in carbon disulphide, is converted to dibenzanthrone by treatment with aluminium chloride at 95-100° for 8.5 hours (118). 4,4'-dibenzoyl-1,1'-binaphthyl is also prepared from 4,4'-dicyanoderivative by saponification with alcoholic alkali at 160-90° in sealed tubes when the dicarboxylic acid is obtained. Changed into the acid chloride and heated with benzene and aluminium chloride for 9 hours at 70-5°, gives the 4,4'-dibenzoyl derivative (119).

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Experimental set-up

Experimental work in the alkali fusion of 2-amino-anthraquinone and benzanthrone required the assembly of two different reactor systems, one was the batch reactor and the other continuous. All preliminary data were collected in the batch reactor which were optimised by statistical methods. On the basis of the results obtained in the batch reactor, a continuous reactor was fabricated which involved considerable efforts in the design, erection and operation.

Batch reactor assembly

A schematic diagram of the batch reactor assembly has been shown in Fig.1.

The reactor was constructed from stainless steel (plate thickness: 3 mm.) and had a capacity of 2.4 litres. It was 200 mm. in height and had a diameter of 125 mm. The reactor top was closed by a stainless steel flange with openings for charging solids, sight glass, gas vent which also could be used as condenser for distillation of naphthalene, and for fixing a thermowell for measurement of temperature inside. A glass thermometer was inserted inside the thermowell for temperature recording. The reactor was provided with an anchor type stirrer made of stainless steel, whose speed could be adjusted by a pulley system run by a 0.5 H.P. motor; the speed was kept constant at 140 r.p.m. during the alkali fusion studies. The heating was done by electrical resistance wire

which was wound on the outside surface of the reactor. By this arrangement a temperature of about 300° could be easily obtained. The radiation losses were minimised by efficient lagging outside. The electrical input was adjusted by means of a variac which controlled the temperature at desired values.

A smaller batch reactor set-up of cast iron was also used while carrying out smaller batch runs. This was gas heated and provided with lagging to minimise radiation losses.

Continuous reactor assembly

The continuous reactor assembly consisted mainly of the following: a reactor tube in the shape of a 'V'; liquid feed arrangement; and solid feed arrangement. A schematic diagram of the assembly is shown in Fig.2.

Reactor

The details of the reactor are shown in Fig.3. The reactor was made of mild steel pipe 55 mm. diameter. The reactor consisted of the following sections: (a) the mixing zone (b) the reaction zone, and (c) the discharge end.

The volumetric capacity of the reactor was 3.3 litres. As the reactants were introduced in the form of solid and liquid, a thorough mixing of both phases was found necessary for efficient reaction. This was done by bulging out the left arm of the V tube to a diameter of 150 mm. A flange was welded at the top in which arrangement was provided for introducing the solid and liquid reactants through separate charging holes. A paddle type

stirrer was provided in both the arms of the 'V'. Both stirrers were driven by two separate 0.25 H.P. motors through V-belts, the speeds of which were maintained at 440 r.p.m. by suitable pulley arrangements.

The temperature of the reaction was measured in two different places at the bottom portion of the V-tube. Separate thermowells were welded inside the V-tube in which glass thermometers were introduced for temperature measurement.

The bottom of the V tube was provided with a stainless steel globe valve for drawing out samples whenever needed.

The discharge hole was situated at the top portion of the right arm of the V-tube. A differential height between the charge and discharge levels facilitated smooth discharge of the product.

The V tube was heated by electric resistance wire as in the case of the batch reactor and was lagged to minimise heat losses. The left and right arms of the V tube were heated separately, the heat input in both arms being controlled by two different variacs. Separate gas heating arrangement was provided at the points where liquid feed was introduced and the discharge of the products. It was found necessary as the molten caustic alkali had a tendency to solidify at these points owing to cooling of the surface.

The products were collected in separate enamel lined mild steel vessels for further processing.

The reactor assembly was fixed on slotted iron stand so that the discharge end was at a height of 1.2 meters from the ground level.

Molten alkali feed arrangement

The liquid feed assembly consisted of an alkali melting vessel of a working capacity of 3 l. (Fig.4b). This was provided with three slanting side discharge holes through one of which molten alkali could be drawn into a measuring device. The side discharge was found necessary as the bottom discharge did not work satisfactorily. The molten alkali contained insoluble impurities like dirt and carbonate which formed a sediment on the top of the valve seat, obstructing thereby the free flow of molten alkali through the valve. This difficulty was completely overcome by the arrangement mentioned above.

The molten alkali was drawn into a measuring device fabricated out of a mild steel pipe of 45 mm. diameter with a conical bottom. The function of this tube was to discharge known quantities of the alkali melt through the bottom valve. The measuring was done in the following manner. At known heights in the tube, open slanting pipes were welded which acted as overflow levels. The bottom valve was first closed, alkali melt was drawn into the tube till part of it overflew through one of the side tubes. The alkali melt contained in the tube was then discharged through the bottom outlet into the V tube reactor. The volume of the alkali discharged was

thus pre-calibrated. The alkali melt in the over-head reservoir and the measuring device was kept molten by providing gas heating and electrical heating respectively.

Solid feed arrangement

The solid feed device employed is shown in Fig.5. This was essentially a screw conveyor, the pitch of the screw being 1/2 in. The screw r.p.m. could be varied by means of a reduction gear and a pulley set. The vessel had a conical cross-section and had a volumetric capacity of about 500 ml. The screw rotated at the bottom of the conical shaped vessel. By adjusting the r.p.m. of the screw, the feed rate could be varied to any desired amount. This device worked well with 2-aminoanthraquinone.

The solid feed consisted of a mixture of 2-aminoanthraquinone and sodium phenolate and the liquid feed consisted of molten alkali containing caustic soda, caustic potash, anhydrous sodium acetate and sodium chlorate. The feed rates of the above reactants could be controlled in the manner described above and the product from the discharge end could be processed in the manner described under batch alkali fusions.

Raw materials and finished products

All raw materials employed in the studies in alkali fusion were analysed to assess their percentage purity. The various methods employed and the results obtained are detailed below.

Analytical techniques

2-aminoanthraquinone

2-aminoanthraquinone was analysed by column chromatography on grade I alumina by the following method (1): about 0.25 gm. of 2-aminoanthraquinone was accurately weighed and dissolved in pyridine and made upto 25 ml. 5 ml. of this solution was chromatographed on alumina grade I column made by wet filling with benzene. The developing solvent mixture consisted of 1 part of pyridine and 3 parts of benzene. The orange red band was eluted into a weighing flask and the solid estimated by evaporating the solvent. The 2-aminoanthraquinone was found to be 98.0 per cent pure.

Caustic soda and potash

The caustic alkalies used were flakes of commercial grade. Their purities were determined by titration with standard potassium hydrogen phthalate solution.

A sample of the phthalate was dried for 1 hour at 100-50°. 0.5 gm. of the phthalate (dry sample) was transferred to a conical flask. 100 ml. of water was added to dissolve to powder completely. Two drops of phenolphthalein were added and the solution was titrated with the alkali solution (0.1 N) taken in the burette.

1 gm. of $COOH.C_6H_4.COOK$ = 0.1959 gm. of NaOH

= 0.2743 gm. of KOH

The purities of the caustic soda and potash were 91.00 and 86.3 percents respectively.

Sodium acetate

Pure anhydrous sodium acetate was used throughout the investigations. The moisture content was estimated and freshly fused sample was used wherever necessary.

The assay in anhydrous sodium acetate was determined by the method described by Rosin (2). About 1.5 gm. of the dry sample was accurately weighed and ignited in a crucible protected from the flame, gently at first, then at a low red heat until thoroughly carbonised. The mass was then cooled, disintegrated and then placed along with the crucible in a beaker. Water (75 ml.) and 0.5 N sulphuric acid (50 ml.) were added and the contents boiled gently for 30 minutes. The contents were filtered and washed with hot water until the washings ceased to redden blue litmus paper. To the cooled filtrate, 2 drops of methyl orange was added and the excess acid titrated with 0.5 N NaOH.

1 ml. of 0.5 N H_2SO_4 = 0.4101 gm. of $NaC_2H_3O_2$

The sodium acetate used was found to have a purity of 98 per cent on drying.

Sodium chlorate

Sodium chlorate of 99 percent purity was used in the investigations.

The assay in the sodium chlorate was determined by the method given below

0.8 gm. of the sample was dissolved in 100 ml. of water. 10 ml. of this solution was transferred to a stoppered bottle and 25 ml. of acid ferrous sulphate solution was added. 25 ml. of potassium iodide solution was then added and the contents were allowed to stand in dark for 1 hour. 50 ml. of water was added and the liberated iodine was titrated with 0.1 N sodium thiosulphate solution. A blank experiment was simultaneously carried out.

1 ml. of 0.1 N $Na_2S_2O_3$ = 0.001775 gm. of $NaClO_3$

Sodium phenolate

Sodium phenolate was estimated by titration with standard sulphuric acid solution.

The percentage purity of sodium phenolate was found to be 90.99.

Sodium hydrosulphite

The analysis of sodium hydrosulphite was carried out as described below [2]. About 1 gm. of the sample was accurately weighed and dissolved in a mixture of 10 ml. of formaldehyde and 10 ml. of water contained in a small glass stoppered flask, and allowed to stand for 30 minutes with frequent agitation.

The solution was then made upto 250 ml. in a volumetric flask with 150 ml. of water and 3 drops of methyl orange solution followed by dropwise addition of 1N sulphuric acid to a slight acid reaction and finally with water. To 50 ml. of the solution 2 drops of phenolphthalein were added followed by just sufficient 0.1 N NaOH to produce a slight pink colour. This was titrated with 0.1 N iodine using starch indicator.

1 ml. of 0.1 N iodine = 0.004353 gm. of $Na_2S_2O_4$

The percentage purity of sodium hydrosulphite was found to be 89.5.

Benzanthrone

The benzanthrone was estimated in the following manner: A sample was accurately weighed and extracted with acetone in a soxhlet apparatus. The extraction was continued till the extract became colourless. The thimble from the apparatus was taken out, dried and weighed. In an example, 0.972 gm. of benzanthrone was extracted which gave 0.861 gm. of the acetone soluble fraction. It was multiplied by a factor 0.975 which gave the amount of benzanthrone which actually went in acetone solvent. The percentage purity of the sample was

$$\frac{100 \times 0.861 \times 0.975}{0.972} = 86.36$$

0.972

Naphthalene

Technical grade naphthalene was found suitable for the alkali fusion studies. It was powdered before use in the reactions.

Evaluation of the dyes

The strengths of the dyes were evaluated by dye trials. The dyeing of indanthrone was carried out at 60°. For 1% shade on 5 g. of cotton yarn the materials requirement were: Indanthrene Blue RSN : 50 mg. NaOH (32%): 4.25 ml. Water (taken initially): 4 ml. Sodium hydrosulphite: 0.5 g. Dispersol (10%): 0.5 ml. Water (subsequently): 91 ml. to make up to 100 ml., MLR being 1:20.

The dye was first vatted at the dyeing temperature (60°) for 20 minutes after which the dyeing was carried out for 30 minutes more. An after treatment was given to the yarns with 5% soap solution (4 ml.), 1% soda ash solution (4 ml.) and glucose: 0.02 gm. to brighten the shades.

The hanks, immediately after dyeing, were washed in cold running water before the dyeings were oxidised.

The comparisons of the dyeing were made with Navinon Blue RSN.

Similar dyeings were carried out for evaluating Indanthrene Dark Blue BO samples.

For 5 g. of the yarn (cotton hank), to get 1% shade, the amounts of the materials used were: Indanthrene Dark Blue BO: 50 mg.; NaOH (32%): 0.25 ml. (initially); Water 4 ml. (initially) and sodium hydrosulphite: 0.1 gm. (initially). Sufficient quantity of Turkey Red Oil was added to the dye to make a paste.

The stock vat was further diluted to a total volume of 100 ml. by the addition of NaOH (32%) : 4 ml. sodium hydrosulphite: 0.4 g., dispersol LT (10%) : 0.5 ml. and water : 91 ml. The MLR was 1:20 as in the case of Indanthrene Blue RSN.

The dyeings were carried out at 55-60° for 30 minutes. After dyeing, the hanks were squeezed and allowed to stand in the air until the shades were fully developed. They were finally soaped at boil.

The yields of indanthrone and dibenzanthrone were based on 130 and 150 per cent strength as compared to standard Navinon dyestuffs taken as 100 per cent.

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CHAPTER-3

RESULTS AND DISCUSSION

Studies in batch alkali fusion of 2-aminoanthraquinone : Effect of process variables

Preliminary experiments

To start with the experiments, a few runs were taken using caustic soda, caustic potash, anhydrous sodium acetate, sodium chlorate and sodium phenolate. The quantities of the reactants used are tabulated in Table (1).

The reactions were carried out in the following manner. Caustic soda, caustic potash and anhydrous sodium acetate (as per quantities given in Table (1)) were charged in the same order into the batch reactor (described in Chapter 2). The contents were first heated to 260° followed by cooling to 200° at which temperature sodium chlorate was carefully added after discontinuing the heating. During the addition of chlorate the stirrer was stopped and care was taken to see that the chlorate did not fall on the blade of the anchor stirrer. Crystalline sodium chlorate was used in preference to the powder brand depending on its availability. The temperature was maintained at 180° and 2-aminoanthraquinone and sodium phenolate added alternatively over a period of 2 hours and, finally, 2-aminoanthraquinone alone (1/6th of the total amount taken) over the next 1/2 hour. During the entire addition of 2-aminoanthraquinone and sodium phenolate, the temperature showed a tendency to decrease first and finally rise to about 200°. The temperature was further

raised to 205° over the next 1/2 hour after which it was discharged into water and processed according to the method described in German literature.

The fusion product was discharged into water kept at 40°. The product remaining in the kettle was separately vatted and added to the main bulk. The contents were then cooled to 48° and vatted at 48°-42° for 1 1/2 hours by addition of sodium hydrosulphite. The leuco indanthrone crystals were filtered in a vacuum filter and washed three to four times with alkaline hydrosulphite solution till the filtrate ran pale brown in colour. The filter cake was then dumped in hot water at 60° and oxidised to the dye at 90° for 3 hours. After cooling, the dye suspension was treated with concentrated sulphuric acid, heated to 60° and filtered hot. The dye cake was washed with a dilute solution of soda ash to remove the acidity and subsequently with hot water followed by a 1% Tamol NNO solution. The cake was finally dried at 100-5°. The strength and quality of the dyes were compared with standard Navinon sample and the yield was reported on 130 per cent strength as described in Chapter 2.

The results of the experiments carried out are reported in Table (2). Under the laboratory conditions, the yield of indanthrone was not at all satisfactory. The method of preparation was, therefore, suitably modified to get substantial yield of the dye and quality product.

The next set of experiments were carried out with the following modifications. While the quantities of the reactants and methods of isolation of the dye remained the same, the preparatory method was altered. An intimate mixture of 2-aminoanthraquinone and sodium phenolate was added to the alkali melt as quickly as possible instead of 2 1/2 hours as in batches 1 and 2. The temperature at which 2-aminoanthraquinone and sodium phenolate were added remained the same at 180°. After completion of the addition, the kettle was heated and the temperature of the contents was raised to 200-5° at which temperature they were held for 1/2 hour to complete the reaction.

The results of these experiments (shown in Table (3)) have indicated definite improvement and the quality of the product was also good.

It was, therefore, necessary to determine the effect of the time of reaction, temperature of reaction, alkali to 2-aminoanthraquinone ratio, sodium phenolate to 2-aminoanthraquinone ratio, and sodium hydrosulphite to 2-aminoanthraquinone ratio on the overall yield of indanthrone. In all these runs the proportions of anhydrous sodium acetate and sodium chlorate were maintained constant at 0.64 and 0.15 parts respectively per part of 2-aminoanthraquinone.

Effect of the time of reaction

The preliminary experiments (described in the previous section) have indicated that carrying out the reaction for 3 hours considerably reduced the yield while it was not affected when the time of reaction was 1/2 hour. A few runs were taken varying the time of reaction with a view to determine the optimum reaction time. The results have indicated that an optimum reaction time was 1/2 hour in which case reasonable yields of the dye were obtained and quality was also good (Table 4)).

Effect of reaction temperature

The alkali fusion reactions were carried out at two different ranges of temperatures: one between 200-5° and the other between 215-20°. The purpose of these experiments was to ascertain the yield and quality of the dye at these temperature levels. The results have broadly indicated that, when the reaction was carried out at 200-5°, the yields and quality of the dyeswere satisfactory (Table 5).

Effect of alkali to 2-aminoanthraquinone ratio

The increase in molten alkali content increased the fluidity of the reaction mass. It was, therefore, decided to study the effect of alkali to 2-aminoanthraquinone ratio. The cost of the vat dye being very high, any variation in the alkali content would not affect its cost to any appreciable extent.

The amount of alkali required for the alkali fusion was gradually cut down to a minimum and its effect on the yield of the dye was evaluated (Table (6)).

When the amount of alkali was cut down to 37.5% of the original value, the yield was not affected appreciably. But during processing, the leuco indanthrone filter cake required more washings by alkaline hydrosulphite solution in order to eliminate the impurities like alizarin and others. The quality of the dye was not good if the washing of the cake was improper.

Effect of sodium phenolate to 2-aminoanthraquinone ratio

The role of sodium phenolate is to act as an anti-frothing agent in the alkali fusion reaction. Due to the high exothermicity and evolution of gases in the reaction, the contents of the reactor always had a tendency to froth out. It was considered worthwhile to determine the optimum requirement of sodium phenolate for smooth reaction. The ratio of sodium phenolate to 2-aminoanthraquinone was varied to different values and the results obtained are summarised in Table (7)).

From the six experiments indicated in Table (7) it could be observed that reduction in the amount of sodium phenolate up to 1/3rd of the original level did not appreciably affect the yield. But in all such cases the batches frothed out. It is, therefore, necessary to add full quantity of sodium phenolate as mentioned in Table (1).

Effect of sodium hydrosulphite to 2-aminoanthraquinone ratio

It was observed that when the product after alkali fusion was dumped in water, the vat dye formed remained in the reduced state to a considerable extent. Consequently the requirement of sodium hydrosulphite as reducing agent was much less than required by theory. The quality of the dye depended mainly on the crystallisation of the leuco dye from the solution. Improper crystallisation resulted in inferior quality of the dye.

A detailed study was therefore made to determine the quantity of sodium hydrosulphite required for crystallisation of the leuco derivative of the dye.

The results obtained in this set of experiments are tabulated in Table (8).

The optimum conditions obtained as a result of the studies with different process variables were established by carrying out few more runs at the optimum level. The optimum level fixed was: (1) reaction time : 30 minutes after the addition of 2-aminoanthraquinone was complete and the temperature reached 200°; (2) reaction temperature : 200-5°; (3) alkali to 2-aminoanthraquinone ratio : 4.32 : 1; (4) sodium phenolate : 2-aminoanthraquinone : : 0.33 parts : 1 part; and (5) sodium hydrosulphite : 2-aminoanthraquinone : : 0.3 part : 1 part.

The results obtained are given in Table (9).

Effect of anionic and non-ionic surface active agents in the alkali fusion of 2-aminoanthraquinone

Investigations were carried out further to study the effect of various surface active agents such as alkyl phenols (or their sulphated products), fatty alcohols (or their sulphated products) and other alkali stable anionic and non-ionic surfactants. In all the previous batch runs carried out, the yield of indanthrone was of the order of 55% or less. Use of sodium phenolate as an anti-frothing agent gave satisfactory results but it was used in large amounts and also presented difficulty in storage and handling due to its hygroscopic and toxic nature. The present studies were directed mainly to use various surface active agents having superior qualities as compared to sodium phenolate and others.

The following surface active agents were used during this investigation: (a) phenolic compounds such as ethylphenols (ortho, meta and para) and its homologues upto dodecyl phenol, o-phenylphenol and p-phenylphenol, bisphenol and compounds of a similar type; (b) fatty alcohols such as lauryl, cetyl, oleyl alcohols and other compounds of a similar type; (c) surface active agents such as metallic stearates (like Al, Pb, Zn, etc.), anionic surfactants like alkylaryl sulphonates with one or more alkyl groups having eight or fewer carbon atoms, disodium-N-octadecylsulphosuccinate, sodium salts or sulphuric acid esters of alcohols having eight or less carbon atoms, sodium salts of sulphuric acid esters having more than eight carbon

atoms, products obtained by sulphonation of secondary alcohols and similar ones, as also non-ionic surfactants such as ethylene oxide condensation products of fatty alcohols, ethylene oxide condensation products of phenolic compounds having an alkyl side-chain, and similar compounds.

The results of the batches using some of the anti-frothing agents listed above are summarised in Table (10).

The use of surface active agents as substitutes for sodium phenolate gave dyes of optimum tinctorial strength and fastness with comparable yields. They were used in smaller amounts as compared to sodium phenolate and were stable and non-toxic. Their advantage over the use of sodium phenolate is well established. The use of various surface active agents (either alone or in combination with sodium phenolate) gave better results as indicated in Table (10).

Studies in the alkali fusion of benzanthrone to dibenzanthrone

This investigation was carried out to study the alkali fusion of benzanthrone to dibenzanthrone. The reaction carried out was as follows: caustic soda (0.81 part) and caustic potash (1.46 parts) were heated together to 260° as in the case of indanthrone and cooled to 220° at which temperature anhydrous sodium acetate (0.214 part) was added. After cooling further to 200°, required amount of naphthalene (as per the amounts needed in each batch) was charged. This was followed by the addition of one of the surface active agents,

(as described in the previous section), wherever necessary, which was 0.05 part per part of benzanthrone. This was followed by the addition of benzanthrone (1 part) at 170° in four equal portions as indicated: first quarter between 170° and 177°; second quarter between 177° and 183°; third quarter at 183-189° and last at 189-195°. The temperature during the addition of benzanthrone was not allowed to go below 160° or above 195° at any stage. As soon as the addition was completed, the contents of the kettle were heated to 208° when distillation of naphthalene started vigorously. The distillation was continued till the temperature reached 220-5°. The amount of distillate collected was about 75-80% of the initial charge of naphthalene. The alkali melt containing the product was then dumped in water (50 parts) in which Kieselguhr (0.5 part) was suspended already. The temperature of the water was kept initially at 54°. The dye was vatted by addition of sodium hydrosulphite (0.38 part) at 68°, under periodic stirring. The product left out in the kettle was separately vatted with a mixture of water (12.5 parts), caustic soda (0.1 part) and sodium hydrosulphite (0.16 part) and this solution, after vatting for some time was also added to the main bulk during filtration. The total vatting time was 2 hours. After completion of vatting, the slurry was filtered in a filter press and the naphthalene cum Kieselguhr cake in the press

was washed with water (20 parts) containing caustic soda (0.1 part) and sodium hydrosulphite (0.16 part). The washings were repeated till the colour of the filtrate turned pale red. The filtrate and the washings were collected and aerated along with open steam to precipitate dibenzanthrone. The dye was then filtered and washed free of the fluorescent substances formed in the reaction and the excess of alkali present.

The first set of experiments were carried out with the following objective. In the alkali fusion runs, excess of naphthalene (2.15 parts per part of benzanthrone) was taken normally and distilled over for re-use in subsequent batches. The distillation of naphthalene used to take a long time and only 80% of the naphthalene charged initially could be recovered. It was therefore planned to perform a series of experiments using only 20% of the naphthalene originally charged and perform the alkali fusion without the distillation of naphthalene. The naphthalene was allowed to reflux at the reaction temperature.

The results are tabulated in Table (12).

The results have indicated that the average yield of dibenzanthrone was 64% (by weight) with the products comparable to standard samples. This yield was far away from the expected yield of about 85%.

It was decided at this stage to employ one of the surface active agents used in indanthrone fusion and study its effects in benzanthrone fusion. The next set of experiments were taken using Tamol NNO (interaction product of naphthalene-2-sodium sulphonate and formaldehyde), the amount taken being 5% on the weight of benzanthrone. The naphthalene as in batches 1 and 2 was allowed to reflux at the reaction temperature. The results obtained are given in Table (13).

Under the circumstances described in batches 3-7 an average yield of 68% was obtained. This also did not indicate substantial increase in the yield of the dye.

It was therefore imperative that the distillation of naphthalene plays an important role in increasing the yield of the dye. To ascertain this, few experiments were carried out using excess of naphthalene (2.15 parts/part of benzanthrone as in Table (11)) and distilling it out. The results have shown marked increase in the yield of dibenzanthrone (Table 14).

Consequently, the optimum requirement of naphthalene was the next factor to be determined. In the batches 8 and 9, the amount of naphthalene taken was 2.15 parts/part of benzanthrone. To ascertain the minimum requirement, it was first cut down to 1.08 parts and later on to 0.753 part (50% and 35%) respectively of the initial amount. The results are summarised in Table (15).

The average yield of dibenzanthrone was 83% (by weight) and the quality was very good.

The next step was to determine two more factors: (a) the possibility of reducing the amount of alkali used in the fusion as in the case of naphthalene and (b) the role of the surface active agents in the fusion. Further runs were taken in the manner described below.

Ine one batch (batch No.12) the naphthalene was taken in the same amount given in the previous batch and excess of it was distilled out. The amount of alkali was also cut down by half (1.14 parts/part of benzanthrone). The reaction was performed for 27 minutes with distillation of naphthalene simultaneously. The yield of the dye was only 22.6% (150 strength and comparable to standard).

In the next few batches naphthalene was completely eliminated. The fusion was done using the surfactant. The amount of the surfactant was 5% on the weight of benzanthrone as in the previous cases. The results are recorded in Table (16). The average yield of dibenzanthrone was 43% only.

The results of the above 20 batches could be summarised as under. The alkali fusion of benzanthrone to dibenzanthrone using excess of naphthalene and distilling it out during the course of the reaction gave excellent yield of the dye with good tinctorial strength. The optimum requirement of naphthalene

was found to be 0.758 part/part of benzanthrone. By using 0.43 part of naphthalene and refluxing it at the reaction temperature, it gave lesser yields of the dye which did not improve to a larger extent even by use of surface active agents. The fusion without naphthalene and using only the surface active agent gave poor yields of the dye.

Studies in continuous alkali fusion reaction

General

The equipment used for the continuous alkali fusion studies and its fabricational details have been described in Chapter 2. Major difficulties were experienced during its fabrication and operation. Originally a device illustrated in Fig.6 was constructed to carry out the reaction. This design was of the type of a 'venuleth dryer' wherein excellent mixing of the solid 2-aminoanthraquinone in the molten alkali medium could be achieved. The assembly fabricated consisted of an overhead tank made out of mild steel which hada volumetric capacity of 22 l. The molten alkali mixture from this tank could be fed into the reactor tube by operating the valve at the bottom. As the capacity of the tank was very large, the flow velocity of the liquid feed through the bottom valve, and consequently the amount of alkali mixture charged would not appreciably change with change in the level of the liquid in the tank. It was found by experiments that the flow velocity of the liquid through the valve did not change more than 5% when 3 litres of the liquid were discharged from the tank when it was filled upto its total capacity.

The reactor (Fig.6) was made out of a mild steel tube 100 mm. in diameter which was closed at both ends by screw caps. A horizontal stirrer with plates welded throughout its full length was held in position at one end over a conical seat which was fixed to one of the screw caps inside. At the other end, the stirrer shaft passed through a horizontal gland and stuffing box arrangement. A three step pulley was fixed to the stirring shaft which was driven by a 0.5 H.P. A.C. motor through a V-belt. The reactor had arrangements for feeding solid and liquid reactants at one end and a product overflow at the other end. The total hold up capacity of the reactor was 2.4 l. after which the contents overflew through the discharge end. At the bottom of the tube a valve was fixed for withdrawing samples at regular intervals and also to empty the reactor for cleaning purposes. The whole unit was mounted on angle iron stand for operation at convenient level.

One of the major difficulties experienced was with respect to the liquid feed arrangement. The device described above was not found suitable for the purpose. The bottom discharge arrangement did not work satisfactorily as the molten alkali contained insoluble impurities which formed a sediment over the valve seat obstructing thereby the flow of molten alkali through the valve. A modified feeding arrangement described in Chapter 2 was found most suitable and it operated well with the molten alkali mixture.

A measured quantity of the molten alkali mixture was fed at regular intervals of 5, 15 and 30 minutes respectively. The amount of alkali fed into the reactor could be varied by employing various overflow levels in the alkali measuring device.

The design of the reactor itself posed many problems. The horizontal stirring shaft passed through a gland and stuffing box. The gland materials could not withstand the molten alkali which resulted in constant leakage through the gland. It was therefore necessary to isolate the gland from the reactants. One way to achieve this was to provide few vertical stirring shafts from the top portion of the reactor tube to agitate the mixture inside. In such a case the medium became very turbulent and the flow through the tube was not smooth. This difficulty was overcome by a design shown in figure 7. The volume of the reactants in this assembly was kept nearly the same as in the horizontal reactor. The glands were not in contact with the molten alkali and were not damaged by it. The solid and liquid reactants were charged in the right arm of the tube and the overflow was collected from the left arm. A bottom discharge valve facilitated withdrawal of samples periodically and also cleaning whenever necessary.

This unit worked satisfactorily but the feeding of 2-aminoanthraquinone presented difficulties. The solid was not mixing well with the molten alkali at the point of feeding. Further, there were stagnant portions of the liquid at the bottom of the reactor due to improper stirring in that area.

The final design (described in Chapter 2) overcame all the difficulties and worked well for the semi-continuous alkali fusion reactions.

A screw conveyor was found to operate well with the 2-aminoanthraquinone. The amount of the solid feed was adjusted by varying the speed of the rotating screw which was also pre-calibrated.

Results of experiments conducted in the V-tube reactor

On the basis of the results obtained from batch alkali fusion reactions in the case of indanthrone, trial runs were taken with a view to study the performance of the continuous reactor.

In the first set of experiments, molten alkali mixture consisting of caustic soda, caustic potash, anhydrous sodium acetate, sodium chlorate and sodium phenolate was charged into the V-tube till the overflow level was reached. The composition of the mixture was the same as in the batch reactions. The melt in the reactor was kept at 200° by regulating the heating. Fresh charges of molten alkali and 2-aminoanthraquinone (92 gm. and 9.5 gm. respectively) were introduced together at regular intervals of 15 minutes. The product was collected after every 2 1/2 hours which was corresponding to 95.0 gm. of 2-aminoanthraquinone feed. The yield of indanthrone was calculated in the usual manner and its quality determined. The results of the first set of eight experiments have indicated a maximum indanthrone yield of 41.2%

The results have indicated the feasibility of utilising this set-up for carrying out the alkali fusion. It, however, did not specify anything regarding the equilibrium conditions in the set up. In order to study this factor, the next series of experiments were carried out in the following manner. The V-tube was filled upto the overflow level with the product obtained from a batch reactor in which equilibrium conditions have already been obtained after 30 minutes of alkali fusion. The product in the V-tube was maintained at 200^{o} before fresh charges of alkali melt and 2-aminoanthraquinone were introduced as in run numbers 1-8. Five runs taken in this manner gave the following results (Table 18).

It was found necessary at this stage to ascertain whether the formation of indanthrone was complete under the above conditions or the product decomposed after formation because of prolonged heating. This was verified by analysing the products obtained after two batch fusions for the indanthrone content. The yields of the dye obtained were 53 and 52% respectively (based on 130 strength).

In order to study the performance of the semi-continuous reactor, ten more runs were taken without interruption over a total period of 25 hours. The products obtained after each 2 1/2 hours period were processed as in batches 1 - 18. The results have indicated an average yield of 48.23% (by weight) (Table 19).

Note: From run number 14 onwards the reactants fed into the V-tube were as mentioned below.

Liquid feed 92.0 gm. (consisting of caustic soda, caustic potash, anhydrous sodium acetate and sodium chlorate) and the solid feed 12.3 gm. (consisting of 2-aminoanthraquinone and sodium phenolate in the same proportion as given in batch reactions). The proportions of the reactants were the same as in the previous runs.

The product from the V-tube reactor weighing 5.805 kg. was processed for indanthrone which gave an yield of 42% based on the 2-aminoanthraquinone charged initially. The strength of the dye was 130 per cent and the quality was good.

Further studies were made to determine the effect of the time of addition of 2-aminoanthraquinone regarding the yield of the product. In the preceding 23 runs the time of addition of 2-aminoanthraquinone and alkali melt (both added together) was at intervals of 15 minutes. The average yield of indanthrone was 48.23%. In the next set of runs the time of addition of both reactants were fixed at 30 minutes intervals. The results obtained (Table 20) gave an yield of 52.34% of theory which was comparable with the batch yield.

The above runs have broadly indicated that lesser yield of indanthrone in runs upto 23 might be due to incomplete reaction of 2-aminoanthraquinone. It was, therefore, decided

to cut down the time of addition to a minimum, i.e. 5 minutes interval. In these runs it was found that, under the existing conditions of mixing, the 2-aminoanthraquinone charged did not mix up well especially during latter runs. The average yield of indanthrone under these conditions amounted to 47.5% (Table 21).

Discussion of the results

The essential feature of this study was to examine the feasibility of designing a unit smaller in size but at the same time efficient in operation. As in the case of batch reactions, good yields were obtained when the reaction time was 30 minutes. In spite of continuous operation over a period of 48 hours, no appreciable decomposition of the dye was observed in the reactor. This suggests the use of the reaction medium in the semi-continuous reactor over a long period. The operation of this unit was very simple and the temperature of the reaction was controllable with ease.

The lack of adequate solid dispersion in the reactor when the time of reaction was reduced to 5 minutes was mainly due to improper arrangement for mixing of solids in the liquid medium. With the exception of this difficulty the performance of the reactor was satisfactory.

The scope of the V-tube reactor's use in other unit processes is very considerable. An ultimate design of such a set up would be one illustrated in Fig.8 wherein a constant level of the products could be maintained as in the V-tube. The overflow of the products in this system would be controlled by the reactants charged into it. This unit could be used for many continuous operations for carrying out sulphonation, nitration and other unit processes.

CHAPTER-4

STATISTICAL DESIGN

The determination of optimum conditions for indanthrone by statistical design

Introduction

The aim of the present investigation is to estimate the best operating conditions for the alkali fusion reaction by maximising the yields of the dye, indanthrone. When the optimum conditions for the maximum yield are far removed from the base level, the method of steepest ascent seems to be the most efficient technique of arriving at the result. As the optimum is approached, the method of local exploration by fitting response surfaces is used so that the optimum could be specified more precisely and the conditions most suitable for practical use determined. The method of Box and Wilson offers a very systematic solution for such problems (1).

An analysis of this type was carried out by Balasubramanian and Doraiswamy (2) (see also reference (3)), employing the German process for the preparation of indanthrone (see chapter 1) wherein the alkali fusion was effected by reacting 2-aminoanthraquinone in an alkali melt consisting of caustic soda, caustic potash, anhydrous sodium acetate and sodium nitrate. The maximum average yield of indanthrone was reported to be 58.4% by weight (based on commercial strength taken as 100%) under the following optimum conditions:

Reaction temperature:	201°
Time of addition of oxidising agent ($NaNO_3$)	50 minutes
Reaction time:	121 minutes
Ratio of 2-aminoanthraquinone to fluxing agent (anhydrous sodium acetate):	55%
Ratio of alkali to 2-aminoanthraquinone:	390%

The process employed in the present analysis essentially differs from the above investigation in that sodium chlorate was used as the oxidising agent and an anti-frothing agent, sodium phenolate, was added during the reaction.

A preliminary analysis of the reaction for the preparation of indanthrone by this process has indicated that a reasonably good yield of about 65% (based on the commercial strength) could be obtained under the following conditions.

Reaction temperature:	190°
Time of reaction:	60 minutes
Weight ratio of alkali to 2-aminoanthraquinone	6 : 1
Weight ratio of sodium phenolate to 2-aminoanthraquinone	0.35 : 1

This process for the alkali fusion is advantageous considering that the time of reaction is short and the yield of the product is better than the previous process.

Method of approach

In practice, a functional relationship exists between one or more quantitative responses such as yield of the product, cost or purity on the one hand and sets of controlled variables like temperature, feed composition, reaction time, etc. on the other. This can be represented mathematically as

$$y = f(x_1, x_2, \ldots\ldots x_k ; \theta_1, \theta_2, \ldots\ldots, \theta_p) \quad \ldots\ldots(1)$$

where

y : yield

$x_1, x_2, \ldots\ldots x_k$: independent variables and

$\theta_1, \theta_2, \ldots\ldots \theta_p$: unknown parameters.

To begin with, however, we do not normally have any knowledge of the nature of the response function. In such cases it can be assumed that the functional relationship is approximated by a polynomial function. Eliminating the higher order terms, we have,

$$y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \text{------} + \beta_k x_k \quad \ldots\ldots\ldots(2)$$

Geometrically it means that the response surface is approximated by a plane in a small experimental sub-region. The slopes of this plane are estimated by performing a suitably arranged set of trials in the sub-region. The relative magnitudes and signs of these slopes calculate the direction of the steepest ascent. This is the direction at right angles to the canteur lines and shows the relative amounts by which the factor should be varied to give a maximum increase in response. The procedure then is

to organise a set of experiments in this direction to re-determine the slopes and this process is repeated. In this way, by a stepwise procedure, optimum conditions can be approached. However, the extrapolation becomes ineffective when second order effects become more significant near the stationary region.

Since the value of the independent variables corresponding to the highest yield would provide an estimate of the optimum level, a polynomial equation is now fitted to the experimental data by the method of least squares through a proper design of experiments. The position of the true maximum occurring within the range considered could then be estimated by differentiating the fitted expression and equating the derivative to zero. When this procedure is generalised for 'k' factors, trials are performed through a grid of points throughout the experimental region and a yield surface is plotted through these points.

One of the striking features to come out of the application of the response surface fitting has been the power of elucidation afforded by analysis of the fitted second degree equation. By reducing the equation to its canonical form, it is possible to interpret the factor dependencies intrinsic to the system under study. The reduction of a second degree equation to canonical form is a standard procedure.

The procedure is to calculate:

1. the position of 'S', the centre of the system of cantours and the value y_s of the response predicted at this point
2. reduction of the equation to the canonical form
3. estimation of the direction cosines of the transformed axis to the original design axis

Application to the preparation of indanthrone

Based on the earlier experiments for the preparation of indanthrone (Chapter 3), the following factors (independent variables) were considered to be of importance.

x_1 : reaction time (after the reactants attain the reaction temperature)

x_2 : reaction temperature

x_3 : weight ratio of mixed alkali to 2-aminoanthraquinone

and x_4 : weight ratio of sodium phenolate to 2-aminoanthraquinone

These were the only variable factors in the investigation keeping the following conditions constant:

1. the time of addition of 2-aminoanthraquinone was two minutes throughout; (After the addition of 2-aminoanthraquinone to the alkali melt the contents of the reactor were brought to the reaction temperature in five minutes in all the runs);

2. the amount of anhydrous sodium acetate was 0.64 part/part of 2-aminoanthraquinone;

3. the quantity of sodium chlorate as the oxidising agent was 0.15 part/part of 2-aminoanthraquinone;

4. sodium hydrosulphite (0.12 part) was added for isolating the product.

The physical factors like the effect of agitation, etc. were not considered in the present investigation.

In the present analysis the response measured was the percentage yield of indanthrone expressed on the basis of 130% strength in comparison to the standard sample taken as 100%.

The levels of factors — x_1, x_2, x_3 and x_4 are given in table 22. In the initial trials, the centre point of this gave an yield close to 52.5%. In view of the expected increase in the yield and consequently the probable remoteness of the starting conditions from the optimum levels, it was felt that the first order effects would be predominant and that higher order effects negligible. A set of eight trials arranged as a half-replicate of a full factorial design was therefore carried out (Table 23). From the theoretical considerations, it was thought that the effects most likely to interact would be x_1 and x_2 and provision was therefore made in the design for the isolation of any interaction between these variables. Thus, no extra factor was associated with the comparison measuring the interaction between x_1 and x_2.

The principal aim being estimation of the first order effects, the fractional factorial design was resorted to in this investigation. The advantage of the factorial design is that the effects could be determined in a simple manner since the least square estimates of the constants are orthogonal linear functions of the observations. Because of this orthogonality each coefficient β may be calculated separately as though this constant is the only one estimated by the data. The estimate of β is given by the simple formula:

$$\beta = \Sigma yx / \Sigma x^2$$

and the variance of β is given by

$$V(\beta) = \sigma^2 / \Sigma x^2$$

where σ^2 is the experimental error variance.

The result of the analysis is given in Table 24.

Estimation of the second order effects

Table 24 shows the estimated slopes calculated on the assumption that the second and higher order effects are small enough to be ignored. However, the significance tests indicate that the second order effects are dominant.

Since the second order effects also had to be determined, a composite design as proposed by Box and Wilson was used.

Composite designs for determining the effects up to the second order are built up from full two-level factorial designs or fractional factorial designs. The procedure is first to choose a two-level design so that all effects of first order and all interaction effects of second order can

be estimated. This design is then supplemented with further points which allow estimation of the quadratic effects. The advantage of composite designs in preference to the three-level factorials is that the second order effects can be estimated with a minimum number of trials without losing the orthogonality and the set of trials can be carried out sequentially.

The results of the composite design are given in Table 25. It can be noted here that this set of trials includes fractional factorial design used for estimating the first order effects. Since it was found that the first order effects were inadequate, it was necessary to embark on the full factorial design and the composite part to estimate the quadratic effects.

The constants for the first order effects and the second order interaction are estimated straightaway by taking advantage of the orthogonality of the design. However, the rest of the second order terms were estimated by employing a slightly different form of the fitted equation. Here,

$$y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{11} x_{11} + \beta_{22} x_{22} + \beta_{33} x_{33} + \beta_{44} x_{44} + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 \quad \ldots(5)$$

where $x_{11} = x_1^2 - \sum x_1^2 / n$, etc. and the estimate of b_o is calculated by

$$b_0 = \bar{y} - b_{11} \Sigma x_1^2 / n, - b_{22} \Sigma x_2^2 /n - b_{33} \Sigma x_3^2 /n - b_{44} \Sigma x_4^2 /n$$

where $\bar{y}$ is the average of all the yields.

The fitted equation in the present case is:

$$y = 50.9 - 0.74x_1 - 0.23x_2 + 0.38x_3 - 0.75x_4 + 1.51x_1^2 + 1.51x_2^2 - 2.96x_3^2 + 0.46x_4^2 - 0.15x_1x_2 + 1.53x_1x_3 - 0.58x_1x_4 + 0.40x_2x_3 - 0.39x_2x_4 \quad ..(7)$$

The 'lack of fit' term which measures the departure of the fitted second degree equation of the true response surface is insignificant in relation to the experimental error. From the previous experience the experimental error variance is estimated to be 1.61 from a set of 5 replicated experiments. This indicates that the above equation can be considered to be the empirical model of the response surface. As such the equation is not very helpful in indicating the effect of the changes in the experiments conditions on the overall yield of the product. The canonical transformation of the variables will, however, simplify the interpretation of the fitted equation.

Canonical transformation

In the canonical transformation, the first step is to estimate the centre of the response surface. The fitted equation is differentiated with respect to each independent variable and the resultant expression is equated to zero. In the matrix notation it is represented as:

$$\begin{bmatrix} 2b_{11} + b_{12} + b_{13} + b_{14} \\ b_{12} + 2b_{22} + b_{23} + b_{24} \\ b_{13} + b_{23} + 2b_{33} + b_{24} \\ b_{14} + b_{24} + b_{34} + 2b_{44} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = - \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \end{bmatrix} \quad ..(8)$$

By solving the above equation, we get

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} = \begin{bmatrix} 0.3036 \\ 0.1919 \\ 0.2715 \\ 1.0714 \end{bmatrix}$$

which are the coordinates of the centre (S) of the response surface and the yield (y_s) at this point is estimated to be 80.4%

The equation is now reduced to the canonical form

$$Y - Y_s = B_{11}X_1^2 + B_{22}X_2^2 + B_{33}X_3^2 + B_{44}X_4^2 \quad .....(9)$$

where B_{11}, B_{22}, B_{33} and B_{44} are the roots of the characteristic equation

$$\begin{bmatrix} b_{11} - B & 1/2\, b_{12} & 1/2\, b_{13} & 1/2\, b_{14} \\ 1/2b_{12} & b_{22} - B & 1/2b_{23} & 1/2b_{24} \\ 1/2b_{13} & 1/2b_{23} & b_{33} - B & 1/2b_{34} \\ 1/2b_{14} & 1/2b_{24} & 1/2b_{34} & b_{44} - B \end{bmatrix} = 0 \quad ..(10)$$

Substituting the proper values and expanding the above equation in the determinant form, we get,

$$B^4 - 0.26\,B^3 - 2.95\,B^2 + 1.54\,B + 0.15 = 0 \quad \text{.....(11)}$$

The roots of this equation are found by the Newton-Raphson method. Accordingly,

$B_{11} = 0.660$; $B_{22} = -0.038$; $B_{33} = 1.456$ and $B_{44} = -1.766$

The canonical form of the original equation is

$$Y - 50.4 = 0.660\,X_1^2 - 0.038\,X_2^2 + 1.456\,X_3^2 - 1.766\,X_4^2 \quad \text{.....(12)}$$

The above equation is the result of the transformation of the type

$$X = M\,(x - x_s) \quad \text{.....(13)}$$

where,

$$[X] = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{bmatrix}$$

$$M = \begin{bmatrix} m_{11} & m_{12} & m_{13} & m_{14} \\ m_{21} & m_{22} & m_{23} & m_{24} \\ m_{31} & m_{32} & m_{33} & m_{34} \\ m_{41} & m_{42} & m_{43} & m_{44} \end{bmatrix}$$

$$(X - X_s) = \begin{bmatrix} x_1 - x_{1s} \\ x_2 - x_{2s} \\ x_3 - x_{3s} \\ x_4 - x_{4s} \end{bmatrix}$$

In the present case,

$$M = \begin{bmatrix} 0.151 & 0.603 & 0.007 & 0.788 \\ 0.465 & 0.061 & 0.358 & 0.020 \\ 0.925 & 0.133 & 0.168 & 0.227 \\ 0.235 & 0.012 & 0.979 & 0.055 \end{bmatrix} \quad \ldots\ldots\ldots (14)$$

$$\text{and } (X_s) = \begin{bmatrix} 0.3036 \\ 0.1919 \\ 0.2715 \\ 1.0714 \end{bmatrix} \quad \ldots\ldots\ldots (15)$$

The yield y may be predicted from equation (12) for any arbitrary set of conditions. The coefficients on the right hand side of equation (12) are negative except the ones for X_1 and X_4. Since only square terms are involved, to maximise y, the other two transformed variables X_2 and X_4 should be set to zero and X_1 and X_3 should be increased. In other words, the level of these factors should be moved away from the origin along the transformed axes X_1 and X_3. It is evident that higher yields are possible by increasing along X_3 than along X_1. A series of experiments along the X_3 axis however failed to show any increase and the yield was constant near its maximum value.

From the above analysis it is clear that the optimum conditions for the alkali fusion of 2-aminoanthraquinone are:

Temperature:	193°
Time:	64 minutes
Alkali:	6.54 parts/part of 2-aminoanthraquinone

Sodium phenolate: 0.403 part/part of 2-aminoanthraquinone

The maximum mean yield at this point was experimentally found to be 53.8% with a standard deviation of 0.055.

References

1. Owen L. Davies, 'The Design and Analysis of Industrial Experiments', Oliver and Boyd, London, 1963

2. S.Balasubramanian, M.Sc.(Tech.) thesis, University of Bombay (1963)

3. S. Balasubramanian, R. Shantaram and L.K. Doraiswamy, Brit.Chem.Engg., 12, No.3, 377-80 (1967)

APPENDICES

TABLES

APPENDICES

Table 1

Material	Mol. Wt.	Quantity (g)	Mole	Molar Proportion	Part by weight
Sodium hydroxide	40.01	81.30	2.03	12.10	2.17
Potassium hydroxide	56.10	242.50	4.32	25.70	6.47
Sodium acetate (anhydrous)	82.04	24.00	0.29	1.74	0.64
Sodium chlorate	106.50	5.50	0.05	0.31	0.15
2-Aminoanthraquinone	223.20	37.50	0.17	1.00	1.00
Sodium phenolate	116.10	12.50	0.11	0.64	0.33
Water (for dumping the product of reaction)	18.02	2250.00	124.80	7432.00	60.01
Water (for washing the kettle)	18.02	250.00	13.87	825.60	6.70
Sodium hydrosulphite	174.10	4.38	0.03	0.15	0.12
Water (during air oxidation)	18.02	1250.00	69.40	412.90	33.34
Sulphuric acid (concentrated)	98.08	16.96 (9.25 ml)	0.17	1.03	0.45
Water (for washing the filter cake)	18.02	562.5	-	-	-
Sodium hydroxide (36° Be')	40.01	30.00	-	-	-
Sodium hydrosulpite	174.10	1.25 (0.625) (subsequently)	-	-	-

Table 2

Batch Number	Time of reaction (hours)	Temperature of reaction (degrees)	% yield of indanthrone	Quality of the dye
1	3	215-20	38	130 strength. Comparable to standard*
2	3	200-5	38	130 strength. Comparable to standard

* Standard : Navinon Blue RSN (Strength 100). After removing water soluble diluents, the standard gave 130 strength.

Table 3

Batch Number	Time of reaction (minutes)	Temperature of reaction (degrees)	% yield of indanthrone	Quality of the dye
3	33	215-20	39	130 strength and close to standard
4	31	215-20	41	130 strength but dull and green
5	38	215-20	40	130 strehgth but brighter than standard
6	34	200-5	50	130 strength and close to standard

Table 4

Batch Number	Time of reaction (minutes)	Temperature of reaction (degrees)	% yield of indanthrone	Quality of the dye
7	62	215-20	40	130 strength. Trifle greener than standard
8	14	215-20	30	130 strength. Slightly duller and greener than standard
9	30	200-5	44	130 strength. Comparable to standard
10	30	200-5	46	130 strength. Comparable to standard
11	30	200-5	45	130 strength. Comparable to standard

Table 5

Batch Number	Time of reaction (minutes)	Temperature of reaction (degrees)	% yield of indanthrone	Quality of the dye
12	30	215-20	40	130 strength. Close to standard
13	37	215-20	40	130 strength. Close to standard
14	45	200-5	53	130 strength. Close to standard
15	38	200-5	52	130 strength. Close to standard

Table 6

Batch Number	Amount of alkali used (%)	Time of reaction (min.)	Temperature of reaction (degrees)	% yield of the dye	Quality of the dye
14	100	45	200-5	53	130 strength. Close to standard
15	100	38	200-5	52	130 strength. Close to standard
16	100	36	200-5	49	130 strength. Greener than standard
17	50	31	215-20	42	130 strength. Close to standard
18	50	31	215-20	45	130 strength. Trifle greener
19	50	36	200-5	41	130 strength. Duller and greener
20	50	34	200-5	49	130 strength Brighter than standard
21	37.5	34	200-5	49	130 strength. Comparable to standard
22	15	21	215	16	130 strength. Slightly greener and duller
23	15	40	222-5	38	130 strength. Comparable to standard
24	15	30	222-5	32	130 strength. Greener

Table 7

In all cases 50% of alkali (4.32 parts/part of 2-aminoanthraquinone) were used.

Batch Number	Amount of sodium phenolate used (%)	Time of reaction (min.)	Temperature of reaction (degrees)	% yield of the dye	Quality of the dye
25	0.33/part per part of 2-amino-anthraquinone (100)	35	200-5	49	130 strength. 'Trifle greener
26	100	30	200-5	49	130 strength Greener than standard
27	100	34	200-5	51	130 strength Greener than standard
28	33.33	32	200-5	39	130 strength Trifle greener
29	33.33	32	200-5	46	130 strength Comparable to standard
30	33.33	32	200-5	49	130 strength Comparable to standard

Table 8

Batch Number	Amount of sodium hydrosulphite added (part)	% yield of the dye	Quality of the dye
14	1.2/part of 2-aminoanthra-quinone	53	130 strength. Close to standard
15	1.2/ -do-	52	130 strength. Close to standard
16	0.12/ -do-	49	130 strength, but greener than standard
27	0.3/ -do-	51	130 strength but greener than standard
31	0.3/ -do-	52	130 strength. Close to standard

Table 9

Batch Number	% yield of the dye	Quality of the dye
32	50	130 strength. Comparable to standard
33	49	130 strength. Comparable to standard
34	51	130 strength. Comparable to standard
35	50	130 strength. Comparable to standard
36	59	130 strength. Comparable to standard
37	57	130 strength. Comparable to standard
38	53	130 strength. Comparable to standard
39	50	130 strength. Comparable to standard
40	52	130 strength. Comparable to standard

Table 10

Batch Number	Anti-frothing agent used	Quantity of the auxiliary (part)	Yidd of indanthrone (%)	Quality of the dye
41	Sodium octyl phenolate	0.17/part of 2-amino-anthraquinone	54	130 strength. Close to standard
42	-do-	-do-	57	-do-
43	-do-	0.083	54	-do-
44	-do-	-do-	54	-do-
45	-do-	0.03	33	-do-
46	Octyl phenol	0.083	57	-do-
47	-do-	-do-	50	-do-
48	-do-	0.03	49	-do-
49	-do-	0.083	51	-do-
50	p-phenyl phenol	0.083	47	-do-
51	o-phenyl phenol	-do-	44	-do-
52	Mixed xylenol	-do-	47	-do-
53	Bisphenol	-do-	50	-do-
54	Lauryl alcohol	-do-	56	-do-

Table 11

Material	Mol.Wt.	Quantity (g)	Mole	Molar proportion	Part by weight
Sodium hydroxide	40.01	238.00	7.12	6.71	0.81
Potassium hydroxide	56.10	511.00	9.11	8.59	1.46
Sodium acetate (anhydrous)	82.04	75.00	0.91	0.86	0.21
Naphthalene	128.00	752.00	5.88	5.54	2.15
Benzanthrone	330.00	350.00	1.06	1.00	1.00
Water (for dumping the product)	18.02	17500.00	970.90	915.40	50.00
Water (for washing the kettle)	18.02	4375.00	241.60	227.80	12.50
Sodium hydro-sulphite (for vatting)	174.00	133.00	0.77	0.72	0.38
Kieselguhr	-	175.00	-	-	0.50
Sodium hydroxide (for vatting left out product from kettle)	40.01	35.00	0.88	0.83	0.10
Sodium hydrosulphite (for vatting left out product in kettle)	174.00	56.00	0.32	0.30	0.16
Water (washing)	18.02	7000.00			
Sodium hydroxide (washing)	40.01	35.00			
Sodium hydro-sulphite (washing)	174.00	56.00			

Table 12

Batch Number	Reaction time (hour)	Reaction temperature (degrees)	% yield of the dye	Quality of the dye
1	3 hours after benzanthrone addition was complete. Addition of benzanthrone: 1 hour	220	60	150 strength Comparable to standard*
2	1 hour after benzanthrone addition was complete. Addition of benzanthrone: 1 hour	220	59	150 strength Slightly greener than standard*
3	1 hour	220	64	150 strength But duller and greener
4	1 hour	215	69	150 strength Close to standard

* Standard - Navinon Dark Blue BO (strength 100). After removing water soluble diluents, the standard gave 150 strength.

Table 13

Batch Number	Reaction time (hours)	Reaction temperature (degrees)	% yield of the dye	Quality of the dye
5	1 1/2 (after benzanthrone addition was complete)	225-30	68	150 strength. Trifle greener than standard
6	1 1/2	225-30	70	150 strength. Close to standard
7	1 1/2	225-30	65	150 strength. Close to standard
8	1 1/2	215	73	150 strength. Close to standard
9	3	225-30	64	150 strength. Close to standard

Table 14

Batch Number	Time of reaction	Temperature of reaction (degrees)	% yield of the dye	Quality of the dye
10	27 minutes after benzanthrone addition was complete	212-5	86	150 strength. Trifle redder than standard
11	3 hours after benzanthrone addition was complete	212-5	83	150 strength. Close to standard

Table 15

Batch Number	Amount of naphthalene taken (part)	Time of reaction	Temperature of reaction (degrees)	% yield of the dye	Quality of the dye
12	1.08 parts/ part of benzanthrone (50%)	1 hour and 52 minutes after benzanthrone addition was complete	208-20	81	150 strength. Slightly redder than standard
13	50%	1 hour and 4 minutes	208-30	81	150 strength. Slightly dull.
14	1.08 parts/ part of benzanthrone (50%)	45 minutes after benzanthrone addition was complete.	208-20	86	150 strength. Close to standard
15	0.75 part/ part of benzan-throne (35%)	26 minutes	208-20	85	150 strength. Close to standard
16	0.75 part/ part of benzan-throne (35%)	36 minutes	208-20	90	150 strength. Close to standard
17	35%	36 minutes	208-20	79	150 strength Close to standard

Table 16

Batch Number	Time of reaction (hour)	Temperature of reaction (degrees)	% yield of the dye	Quality of the dye
18	1	208-20	45	150 strength. Close to standard
19	1	208-20	40	150 strength, but duller than standard
20	1	208-20	43	150 strength. Close to standard

Table 17

Run Number	Weight of product collected (g)	Yield of indanthrone (g)	(%)	Quality of the dye
1	1216	6	6	130 strength. Comparable to standard
2	987	12	11	-do-
3	1103	12	11	-do-
4	1090	19	18	-do-
5	834	18	17	-do-
6	961	30	28	-do-
7	1440	44	41	-do-
8	1209	42	39	-do-

Table 12

Batch Number	Weight of product collected (g)	Yield of indanthrone g	%	Quality of the dye
9	652	27	29	130 strength. Comparable to standard
10	1023	40	43	-do-
11	988	37.5	41	-do-
12	1448	50	54	-do-
13	903	31	34	-do-

Table 19

Run Number	Weight of product collected (g)	Yield of indanthrone g	Yield of indanthrone %	Quality of the dye
14	1367	55	64	130 strength. Comparable to standard
15	1210	42	49	-do-
16	1077	46	54	-do-
17	1077	38	44	-do-
18	1362	52	61	-do-
19	1121	38	44	-do-
20	992	32	38	-do-
21	1095	35	41	-do-
22	1221	37	43	-do-
23	1216	37	43	-do-

Table 20

Run Number	Weight of the product collected (g)	Yield of indanthrone g	Yield of indanthrone %	Quality of the dye
24	1200	49	57	130 strength. Comparable to standard
25	1127	42	49	-do-
26	863	29	34	-do-
27	1195	40	47	-do-
28	1296	53	62	-do-
29	1167	47	55	-do-
30	1364	50	59	-do-
31	1159	40	47	-do-
32	1133	52	61	-do-
33	1200	49	57	-do-
34	1127	42	49	-do-
35	1195	40	47	-do-

Table 21

Run Number	Weight of the product collected (g)	Yield of indanthrone g	%	Quality of the dye
36	1470	41	43	130 strength. Comparable to standard
37	1217	43	50	-do-
38	1214	35	41	-do-
39	1167	35	41	-do-
40	963	31	36	-do-
41	1038	58	68	-do-
42	936	41	48	-do-

Table 22

	Factor levels		Basic level
	+ 1	- 1	0
Reaction temperature (degrees)	200	180	190
Reaction time (minutes)	80	40	60
Amount of alkali (Part)	8	4	6
Amount of phenolate (Part)	0.4	0.3	0.35

Coded Variables

$$x_1 = \frac{\text{Reaction temperature (c)} - 190^{\circ}}{10}$$

$$x_2 = \frac{\text{Reaction time (min.)} - 60 \text{ min.}}{20}$$

$$x_3 = \frac{\text{Amount of alkali (Part)} - 6 \text{ Parts}}{2}$$

$$x_4 = \frac{\text{Amount of phenolate (Part)} - 0.35 \text{ Part}}{0.5}$$

Table 23

Trial	Factor Level (x_1)	(x_2)	(x_3)	(x_4)	Yield (%) (y)
1	+1	-1	-1	-1	43.9
2	+1	+1	-1	+1	45.7
3	+1	-1	+1	+1	51.0
4	+1	+1	+1	-1	53.1
5	-1	-1	-1	+1	54.1
6	-1	+1	-1	-1	53.1
7	-1	-1	+1	-1	52.6
8	-1	+1	+1	+1	53.7

Table 24

Constant estimated (1)	Σx_2 (2)	Σyx (3)	Estimate (3)/(2)	Component sum of squares $(3)^2/(2)$
b_o	8	404.1	50.51	20412.10
b_1	8	-1.1	-0.14	0.27
b_2	8	-6.7	-0.84	5.61
b_3	8	8.5	1.06	9.03
b_4	8	-11.2	-1.4	18.68
			Deviation from regression:	851.47
			Total:	21,297.16

Table 25

Trial Number	Factor levels				Yield (y)
	x_1	x_2	x_3	x_4	
1	- 1	- 1	- 1	- 1	53.1
2	+ 1	- 1	- 1	- 1	48.9
3	- 1	+ 1	- 1	- 1	53.1
4	+ 1	+ 1	- 1	- 1	51.5
5	- 1	- 1	+ 1	- 1	52.6
6	+ 1	- 1	+ 1	- 1	54.7
7	- 1	+ 1	+ 1	- 1	53.7
8	+ 1	+ 1	+ 1	- 1	53.1
9	- 1	- 1	- 1	+ 1	54.1
10	+ 1	- 1	- 1	+ 1	49.4
11	- 1	+ 1	- 1	+ 1	51.0
12	+ 1	+ 1	- 1	+ 1	45.7
13	- 1	- 1	+ 1	+ 1	51.5
14	+ 1	- 1	+ 1	+ 1	51.0
15	- 1	+ 1	+ 1	+ 1	53.7
16	+ 1	+ 1	+ 1	+ 1	51.5
17	$-\alpha_1$	0	0	0	51.5
18	$+\alpha_1$	0	0	0	53.1
19	0	$-\alpha_2$	0	0	53.1
20	0	$+\alpha_2$	0	0	51.5
21	0	0	$-\alpha_3$	0	45.7
22	0	0	$+\alpha_3$	0	40.4
23	0	0	0	$-\alpha_4$	54.7
24	0	0	0	$+\alpha_4$	53.1
25	0	0	0	0	49.9

Table 26

Constant estimated	Degree of freedom	Estimate	Component sum of squares	Mean sum of squares
β_0	1	50.9	65,828.038	65,828.038
β_1	1	-0.735	10.804	10.804
β_2	1	-0.225	1.124	1.124
β_3	1	-0.375	2.812	2.812
β_4	1	-0.750	11.250	11.250
β_{11}	1	1.51	7.410	7.410
β_{22}	1	1.51	7.410	7.410
β_{33}	1	-2.96	28.470	28.470
β_{44}	1	0.460	0.688	0.688
β_{12}	1	-0.150	0.450	0.450
β_{13}	1	1.530	46.820	46.820
β_{14}	1	-0.525	5.512	5.512
β_{23}	1	0.400	3.200	3.200
β_{24}	1	-0.390	3.042	3.042
β_{34}	1	0	0	0

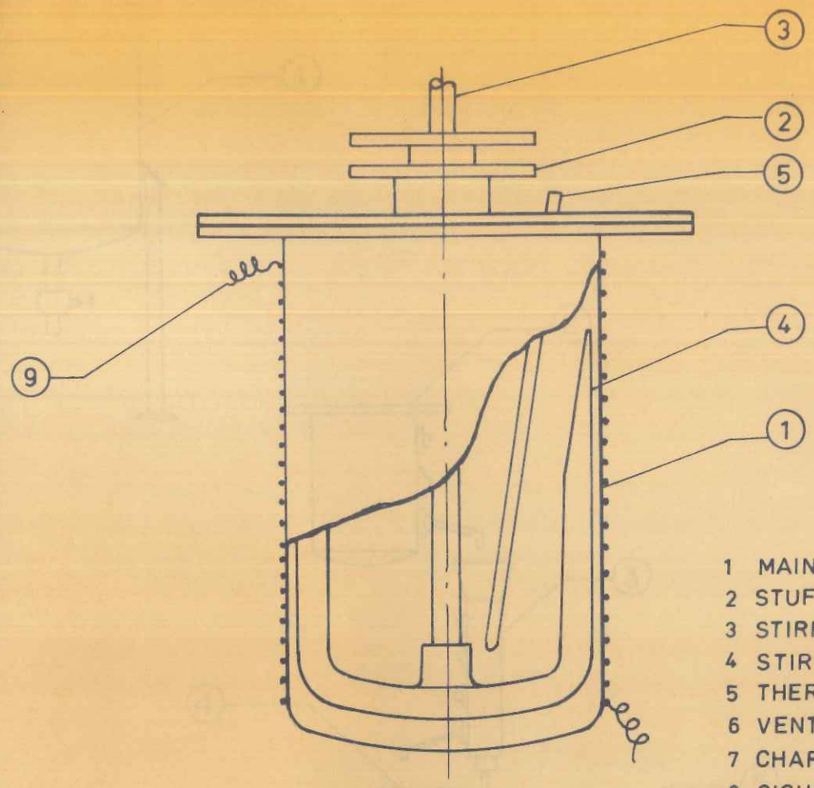
Deviation from regression = 32.53
(Degrees of freedom = 10)

Total: 65,957.560

Variance ratio of deviation from regression to experimental error 2.02

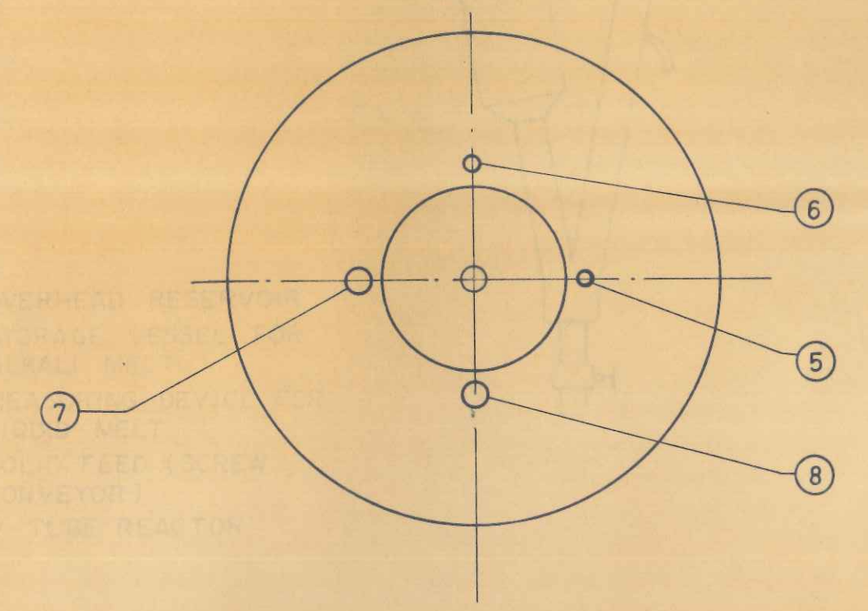
$F_{(10,4)}$ at 95% confidence level 5.96

FIGURES



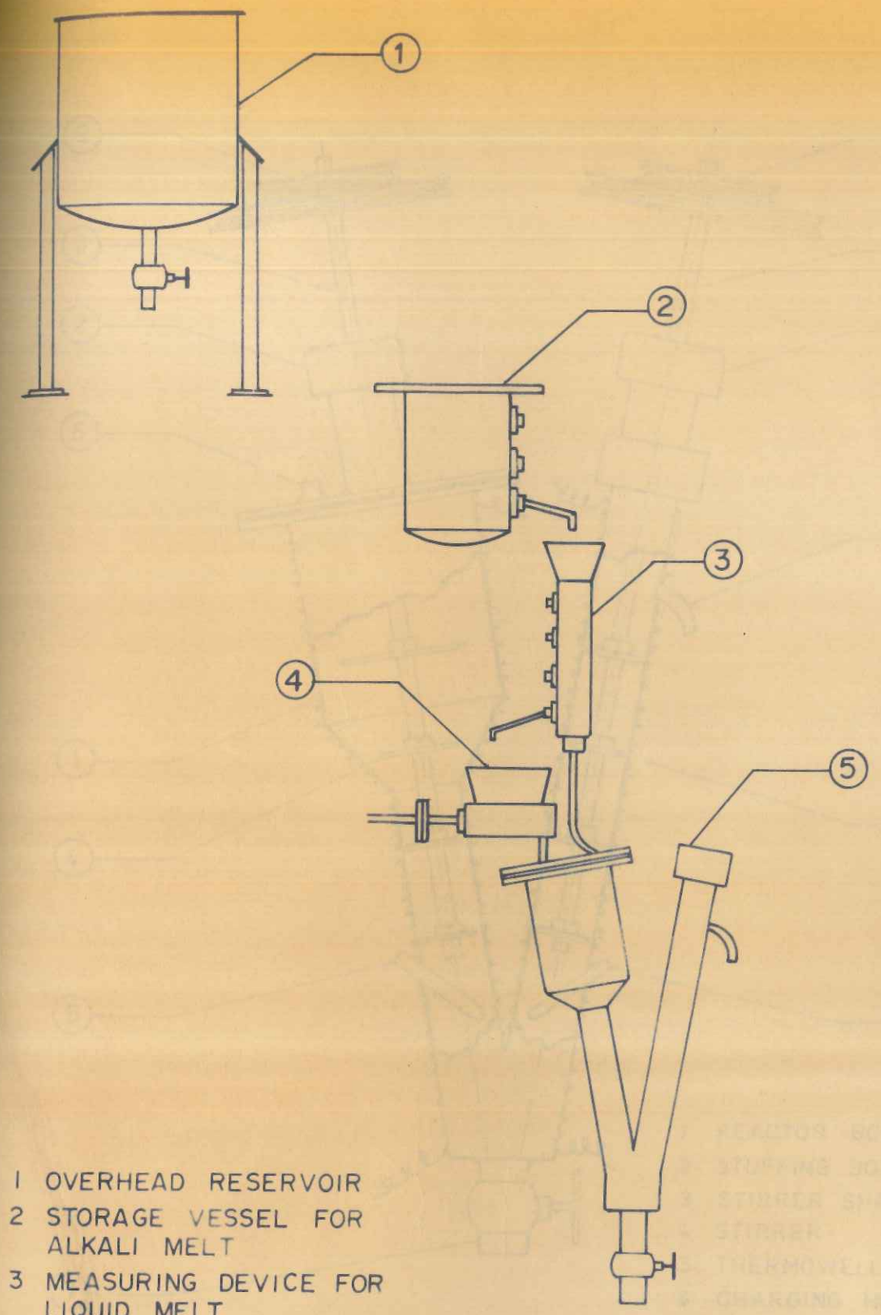
ELEVATION

1 MAIN BODY, 200 x 125 Ø
2 STUFFING BOX
3 STIRRER SHAFT
4 STIRRER
5 THERMOWELL
6 VENT
7 CHARGING HOLE
8 SIGHT GLASS
9 ELECT. RESISTANCE WIRE



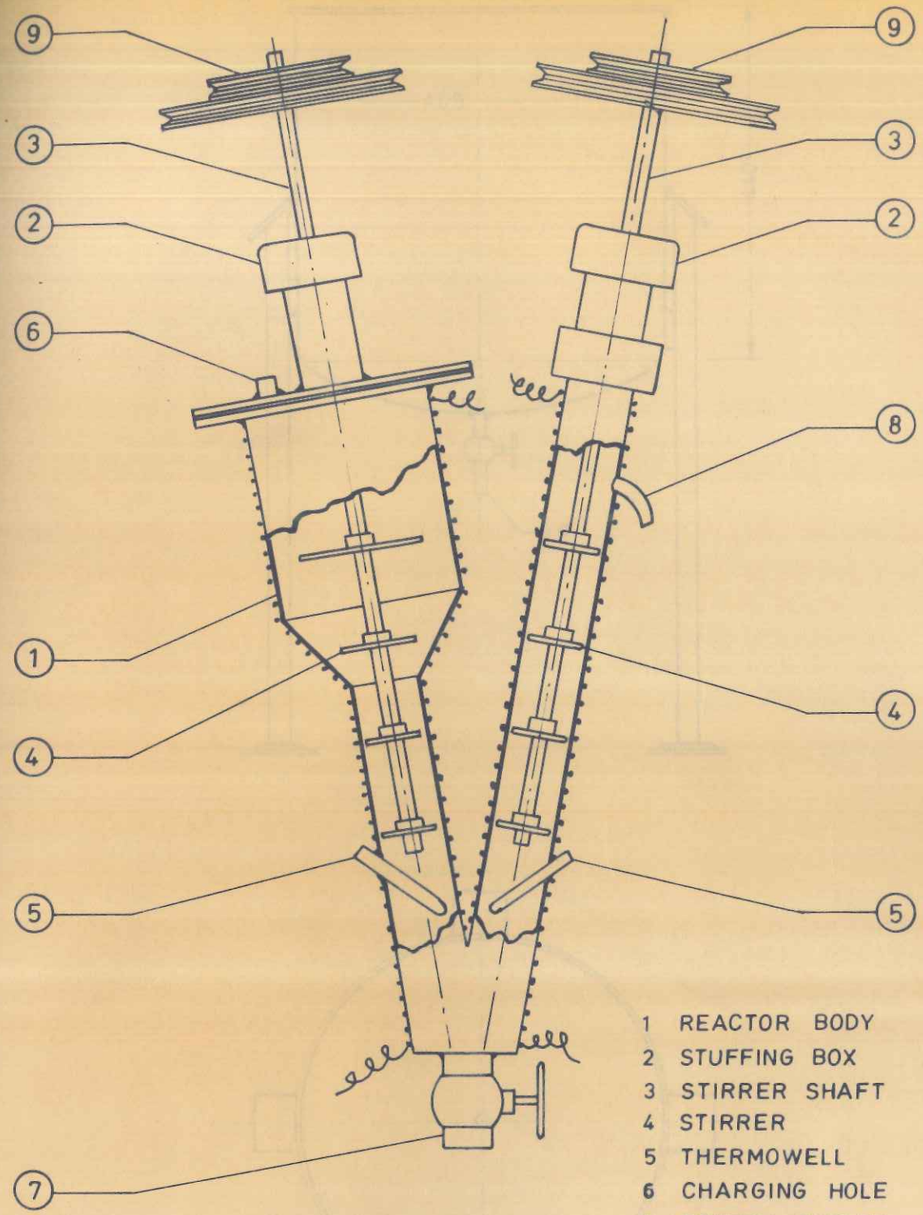
PLAN

FIG. 1. BATCH REACTOR ASSEMBLY



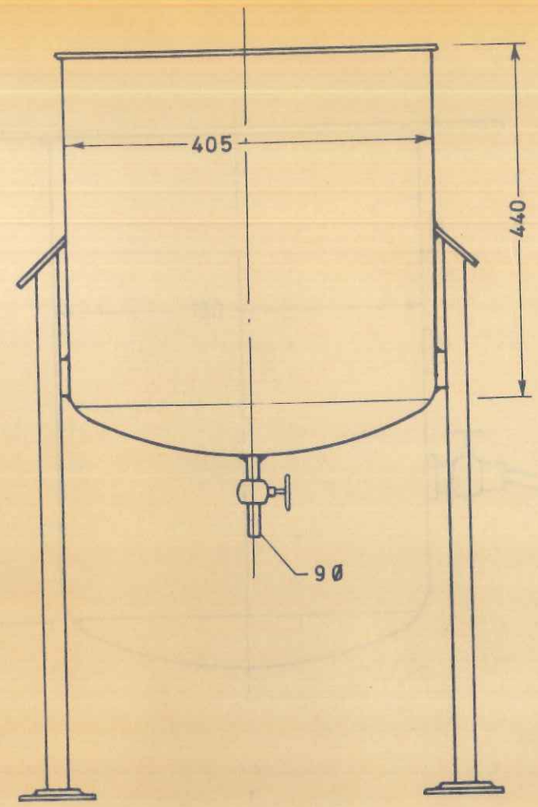
1 OVERHEAD RESERVOIR
2 STORAGE VESSEL FOR ALKALI MELT
3 MEASURING DEVICE FOR LIQUID MELT
4 SOLID FEED (SCREW CONVEYOR)
5 V-TUBE REACTOR

FIG. 2. SEMI-CONTINUOUS REACTOR ASSEMBLY.



1 REACTOR BODY
2 STUFFING BOX
3 STIRRER SHAFT
4 STIRRER
5 THERMOWELL
6 CHARGING HOLE
7 BOTTOM OUTLET
8 OVERFLOW
9 STEP PULLEY

FIG. 3. V-TUBE REACTOR - DETAILS



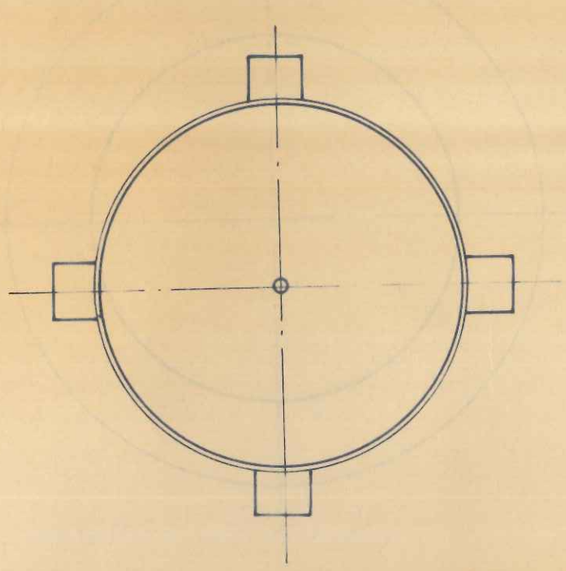
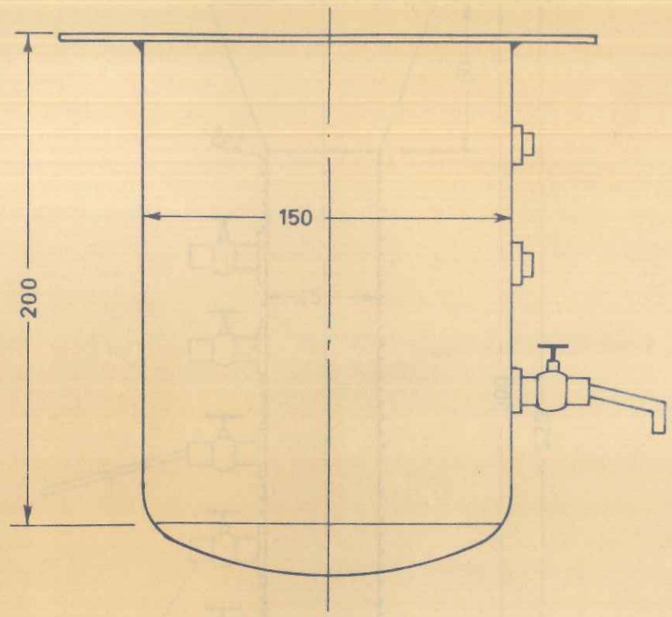


FIG. 4a LIQUID FEED RESERVOIR



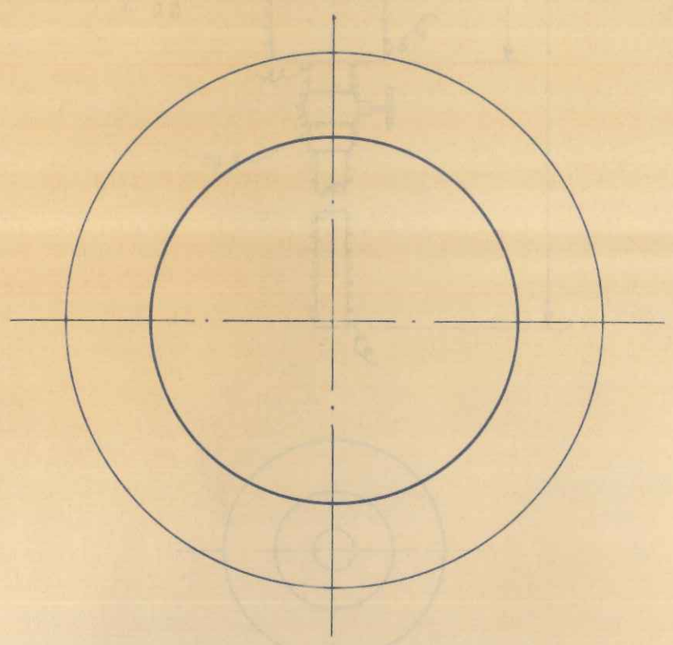


FIG. 4b. LIQUID FEED

(STORAGE VESSEL)

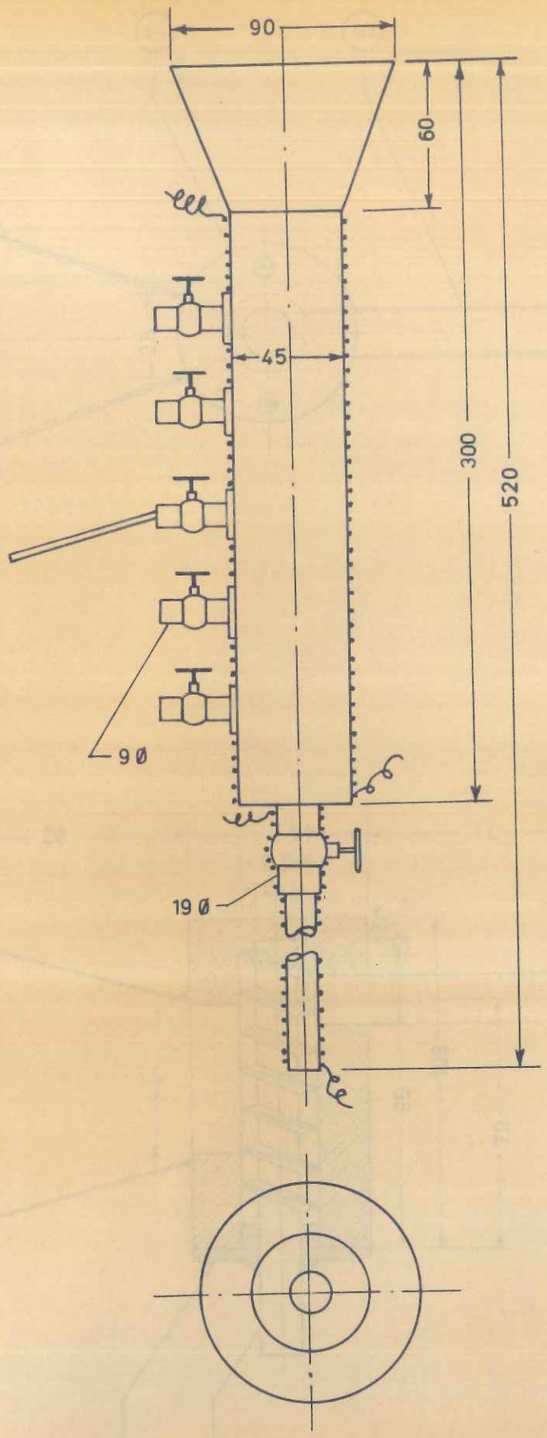
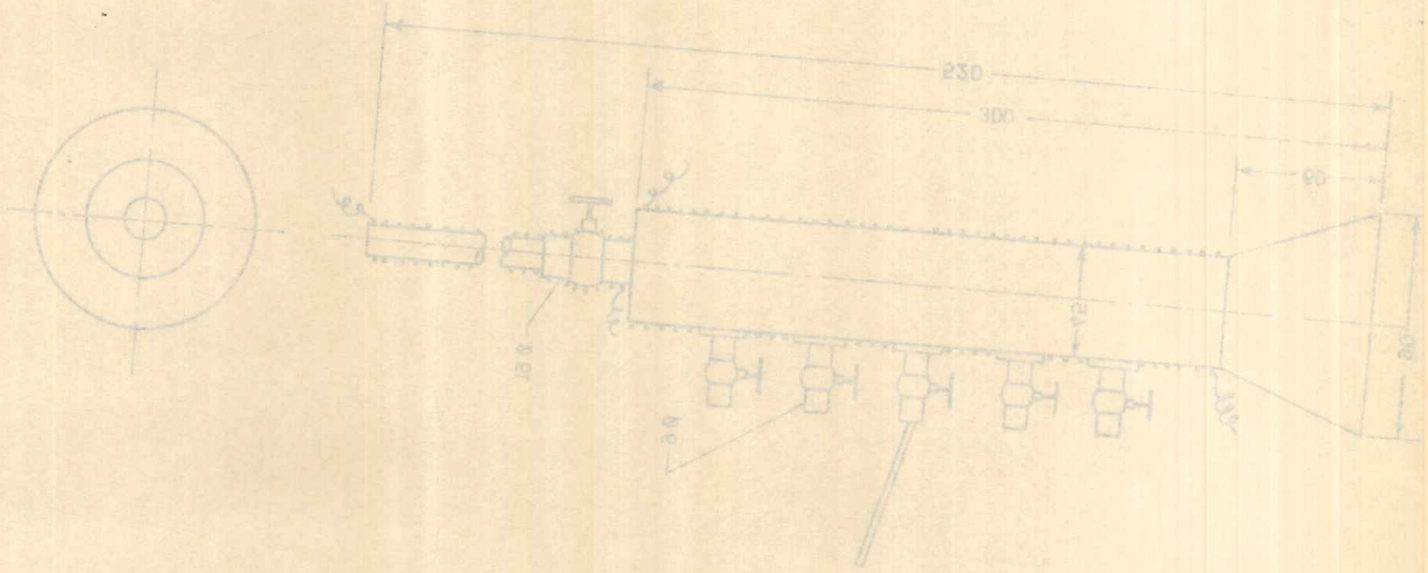


FIG. 4c. LIQUID FEED MEASURING DEVICE



1 HOPPER
2 BODY, 44 Ø
3 SCREW, 22 Ø
4 CAP, 22 Ø
5 OUTLET, 15 Ø

SOLID FEED

SCREW CONVEYOR TYPE

FIG.- 5.

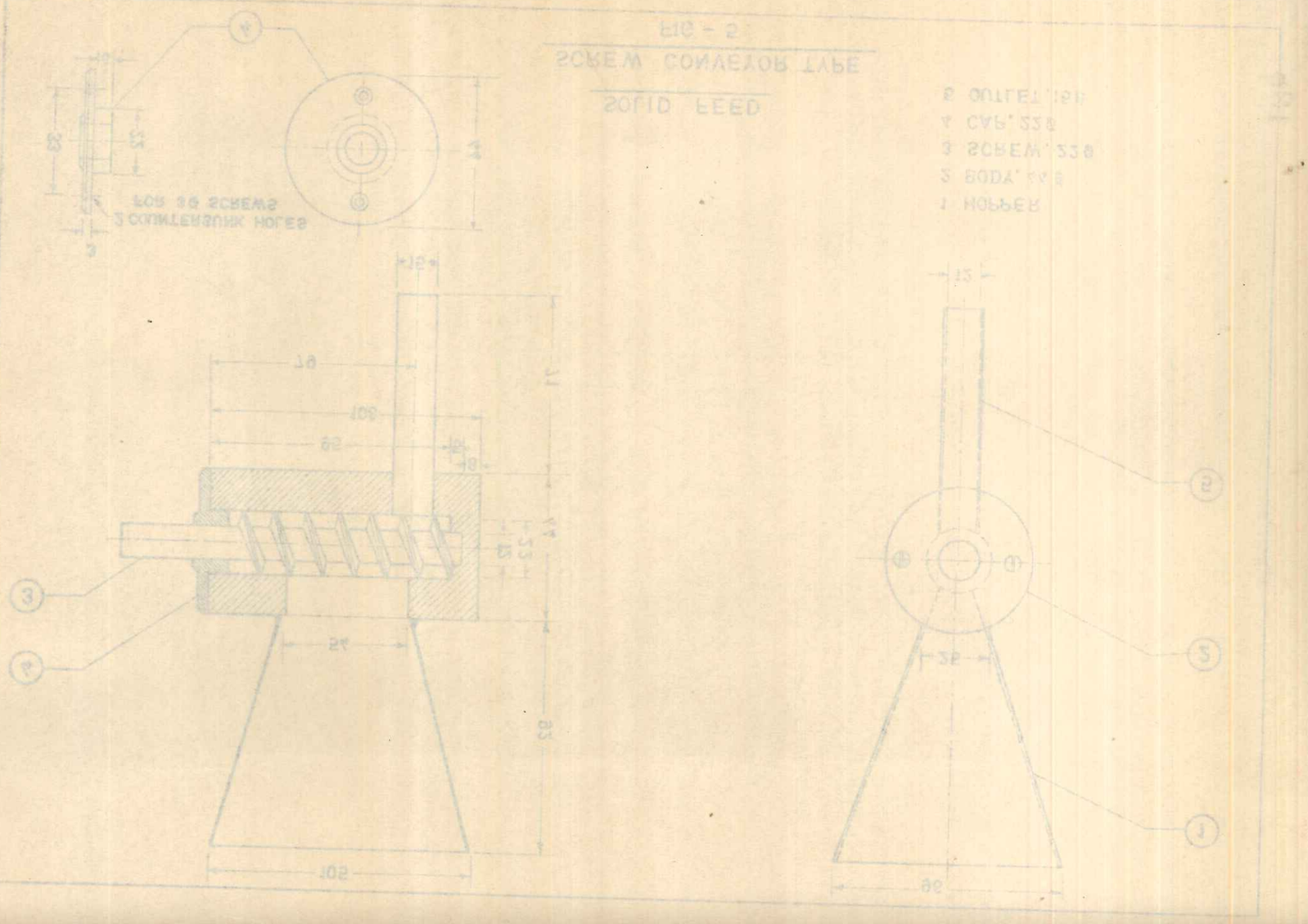
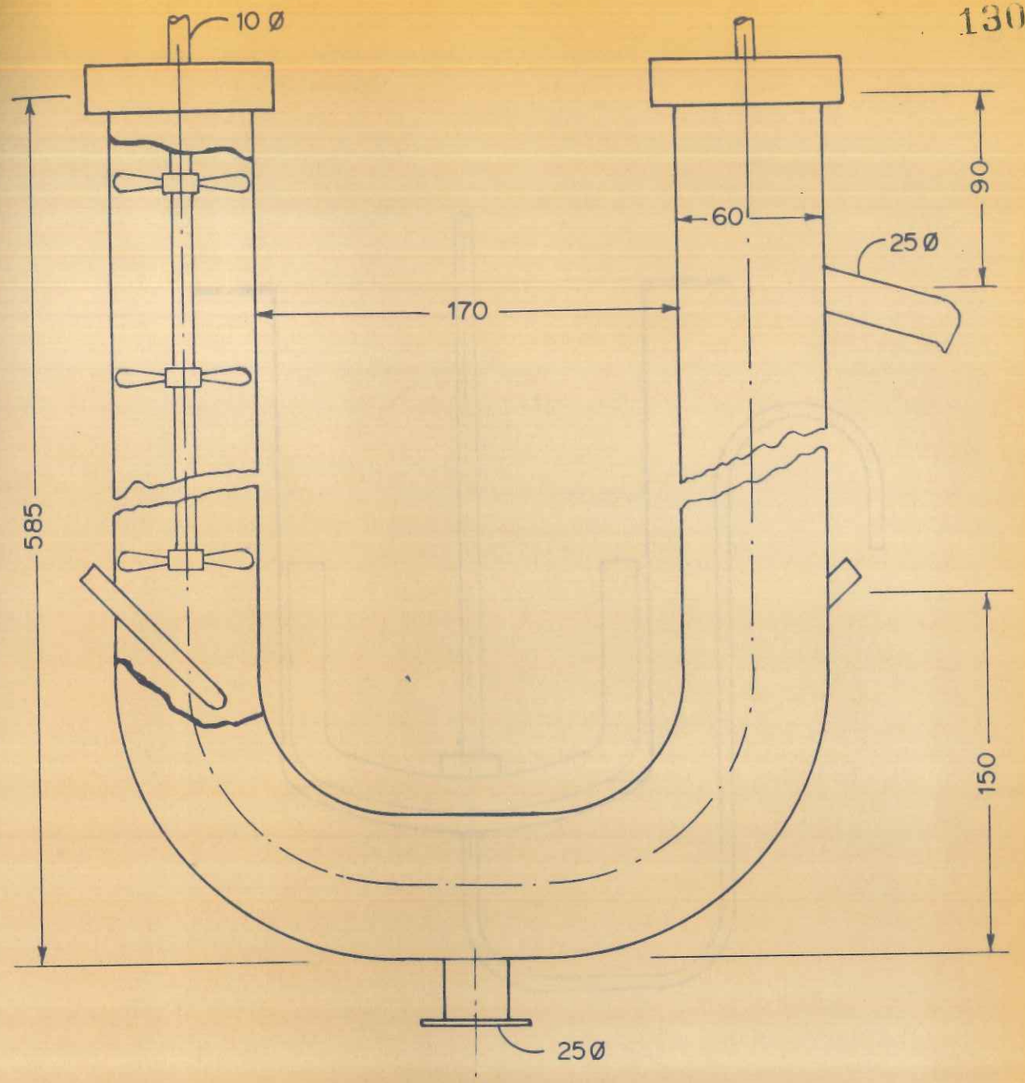


FIG. 6. CONTINUOUS REACTOR – HORIZONTAL TUBE



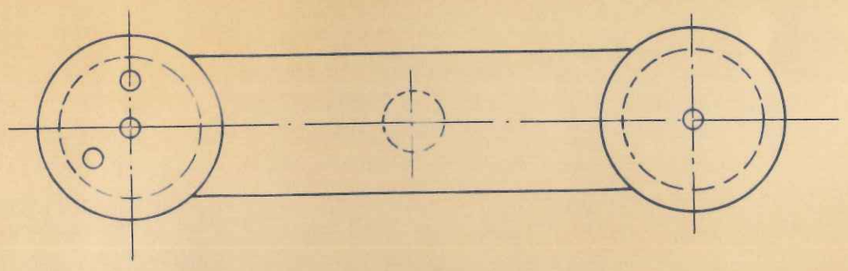


FIG. 7. 'U' TUBE REACTOR

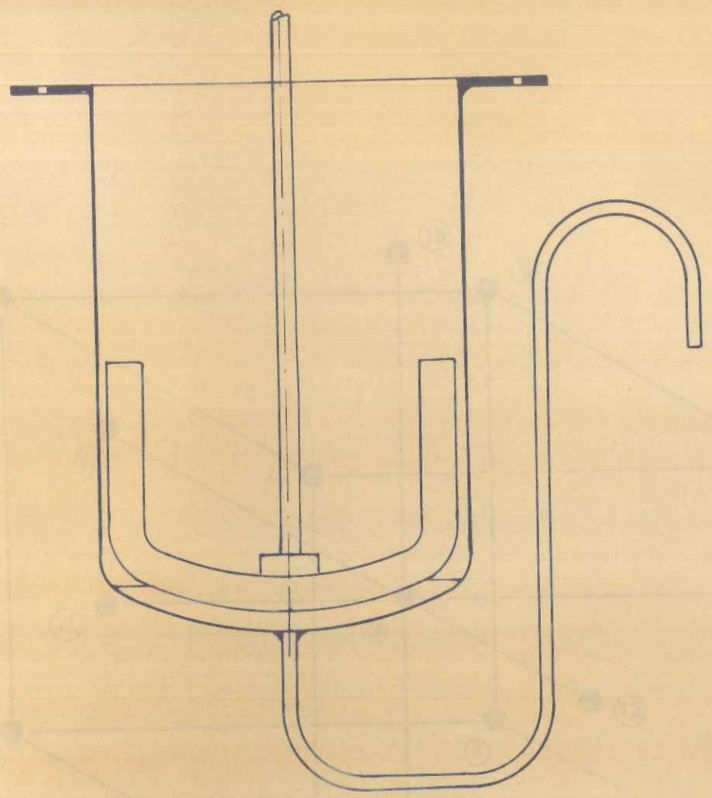


FIG 8. REACTOR FOR CONTINUOUS AND SEMI-CONTINUOUS FUSIONS

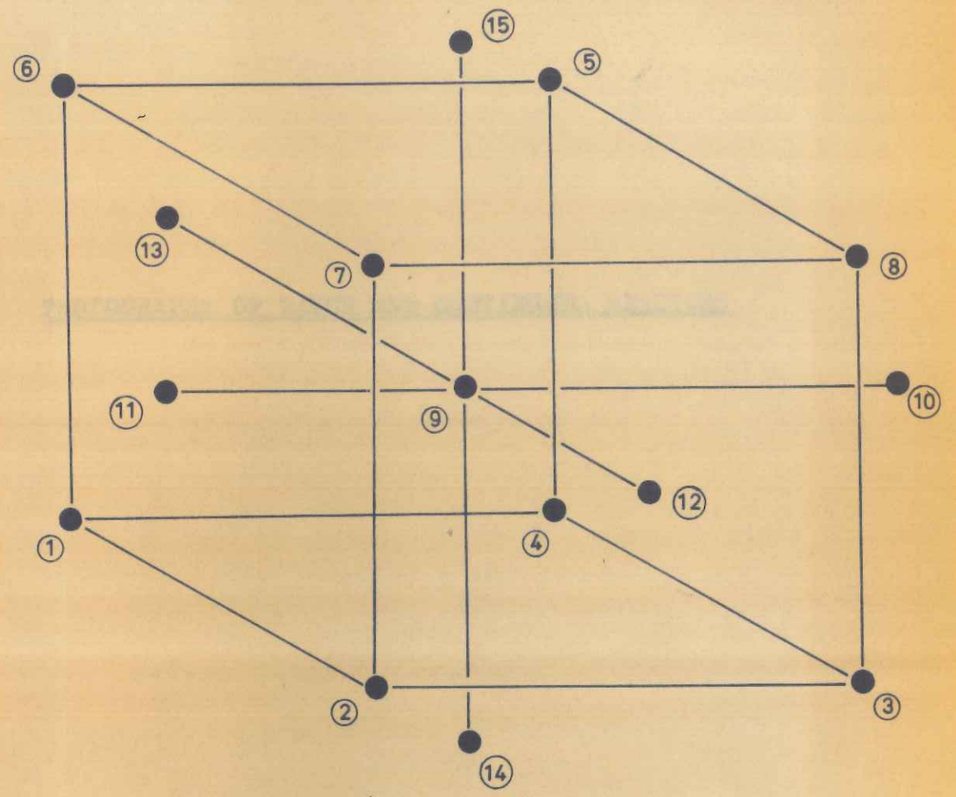


FIG. 9.

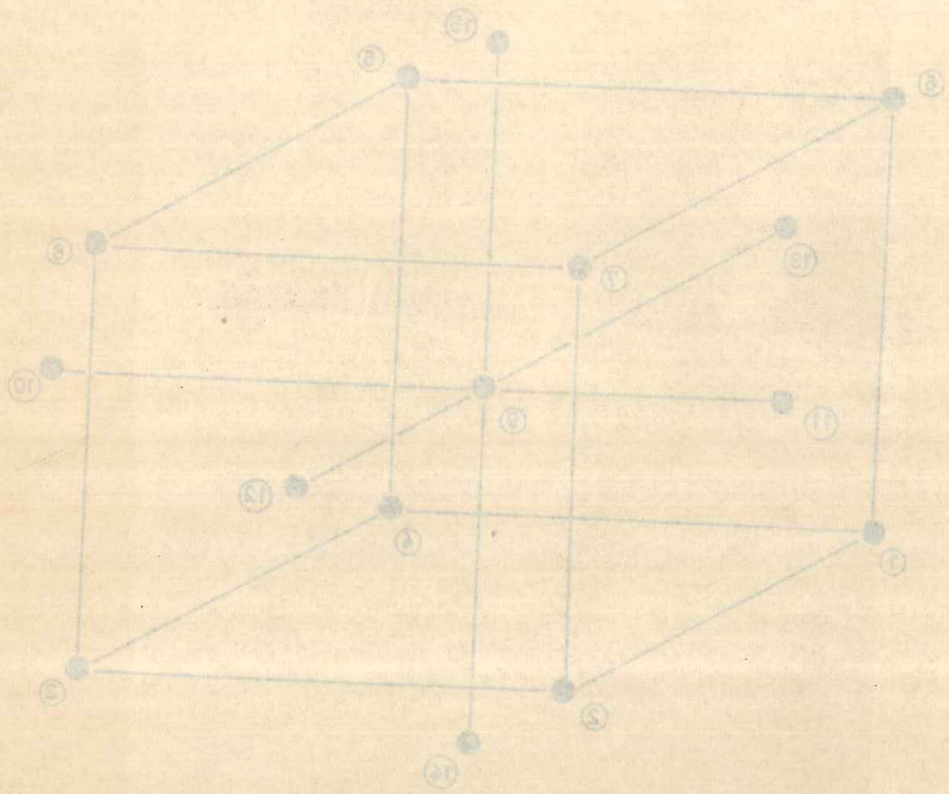
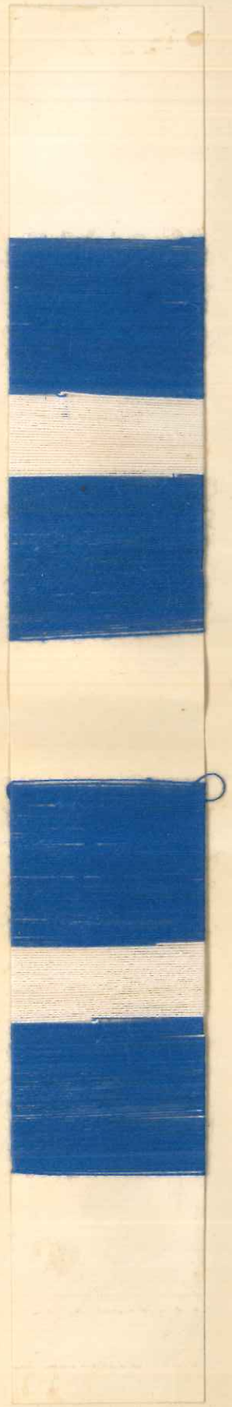


FIG. 9.

PHOTOGRAPHS OF BATCH AND CONTINUOUS REACTORS

DYED SAMPLES

DYED SAMPLES

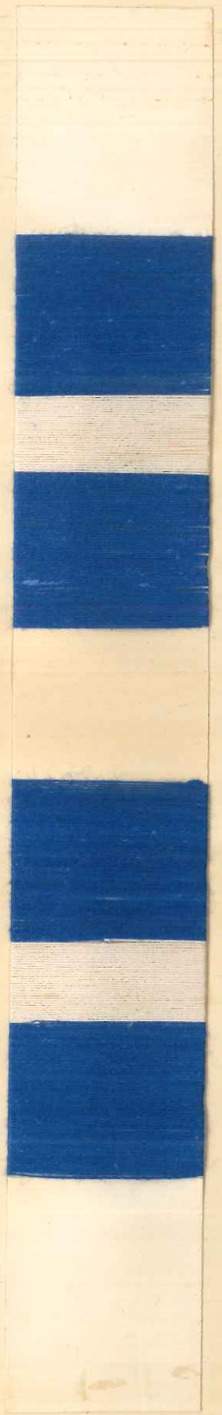


Navinon Blue RSN
Standard - 130% strength

Batch No.6 (using sodium phenolate)
100% strength

Navinon Blue RSN
Standard - 130% strength

Batch No.42 (using surfactant)
100% strength

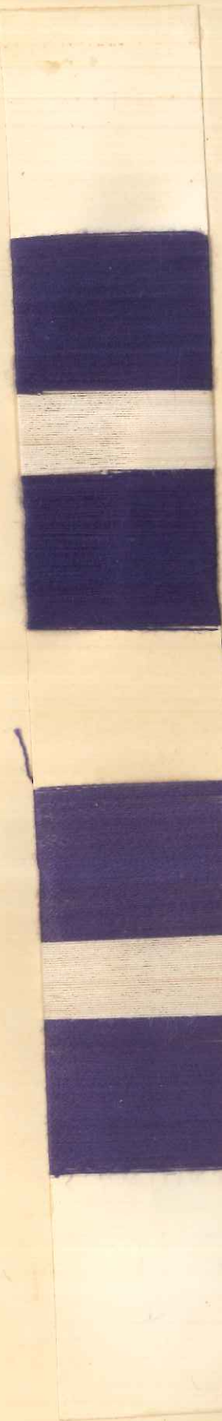


Navinon Blue RSN
Standard - 130% strength

Statistical batch No.1
100% strength

Navinon Blue RSN
Standard - 130% strength

Run No.36 (semi-continuous reactor)
100% strength



Navinon Dark Blue BO
Standard - 150% strength

Batch No.9
100% strength

Navinon Dark Blue BO
Standard - 150% strength

Batch No.19 (using
surfactant)
100% strength

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Candidate

Due date	Due date

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Due date	Due date

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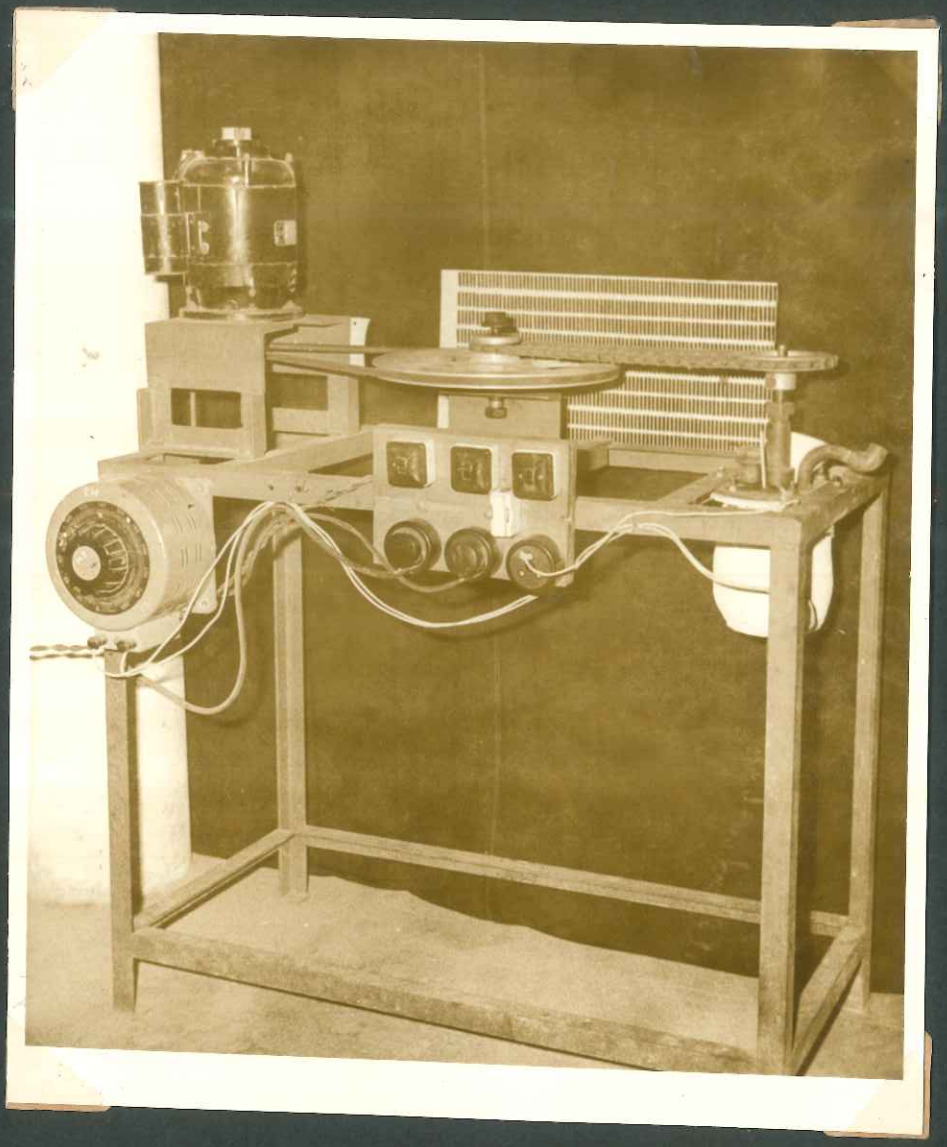
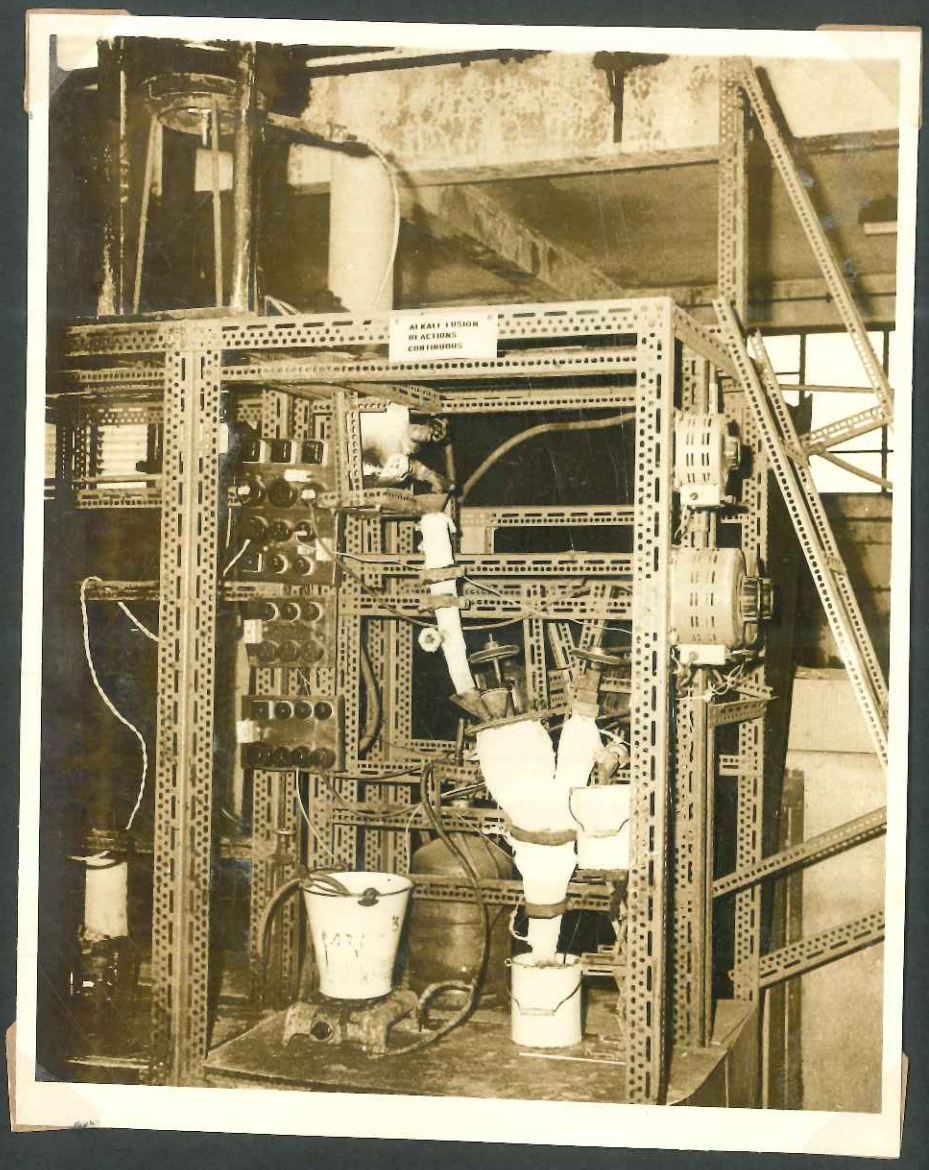
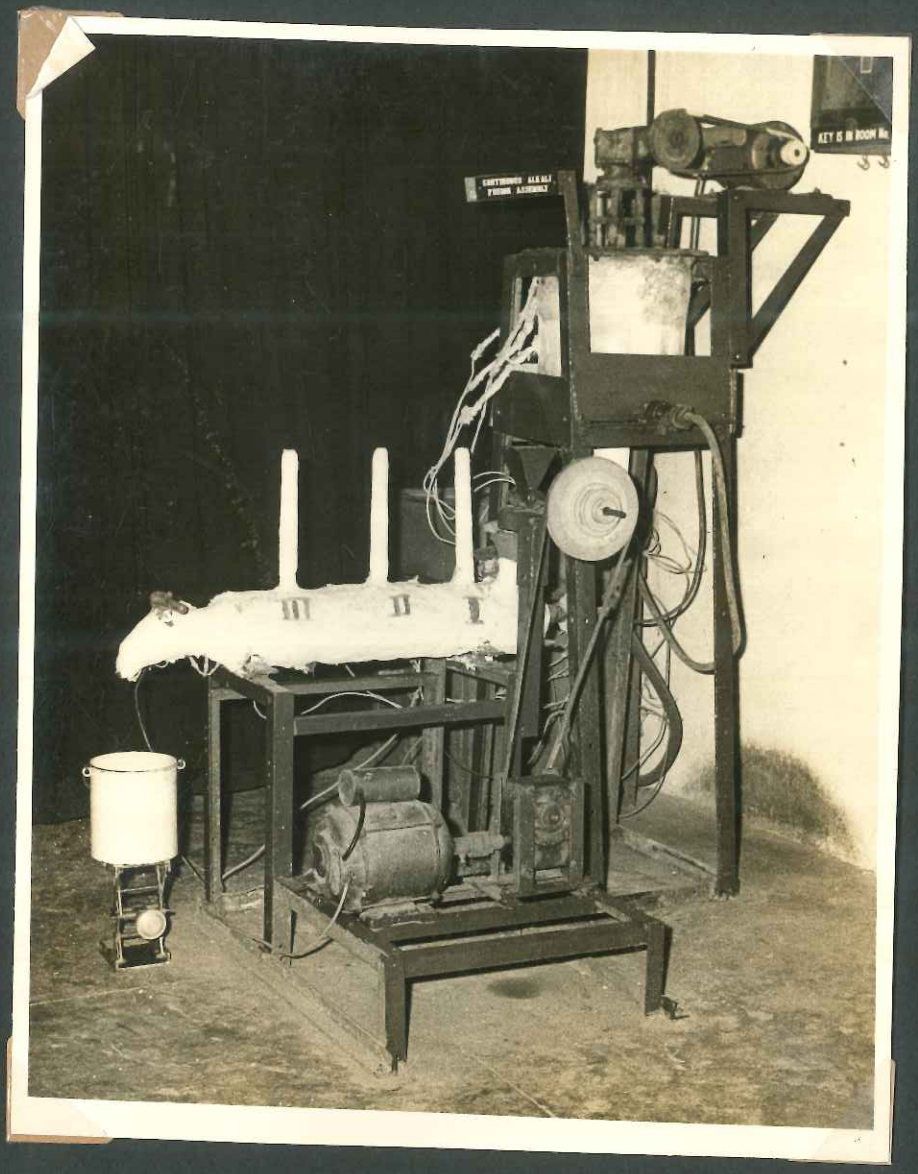


Batch Reactor Assembly



V-Tube Reactor



Continuous Reactor -
Horizontal Tube