CENTRAL INTELLIGENCE AGENCY

INFORMATION REPORT

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COUNTRY	USSR (Voroshilovgrad Oblast)	REPORT NO.	[redacted] 25X1
SUBJECT	Research on Organic Dye Stuffs at the Rubezhnoye Chemical Combine	DATE DISTR.	3 November 1953
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1. The Rubezhnoye (N 49-01, E 38-23) Chemical Combine produced, principally, organic dye stuffs, intermediate products, and some base materials. The plants, built by American firms in 1926, were partly dismantled during World War II and the buildings were heavily damaged. From 1946 [redacted] reconstruction was slow. For example, the power station which had been under construction as early as 1946 had not been completed [redacted] 25X1 25X1

2. The manager of the Combine, not a specialist, was a State or Party functionary who directed not only the works but also most of the provision and clothing shops, hotels, culture buildings, and other installations in Rubezhnoye. The technical manager of the Combine was the chief engineer who was the supervisor of department and shop managers. [redacted] the laboratory of the German specialists employed in the works was directed by Bulkin (fnu), a rather young Soviet chemist, who was afterward sentenced to several years of penal servitude for unknown reasons. He was succeeded by Viktor Yemilyevich Reynfart, a Moscow chemist who was given the title of director after the laboratory had been taken over by the NIOPIK (nauchny institut organicheskikh produktov i krasitelyey - Scientific Institute for Organic Products and Dye Stuffs). Second to Reynfart, who was a high-ranking Party functionary, was Deputy Director Troyanov (fnu) who had been awarded a Stalin prize for scientific works in 1951 and who directed the works of the German research team. Soviet personnel of the laboratory included two women secretaries, a woman bookkeeper, a woman librarian, and three workmen. Several Soviet chemists and women assistant chemists were assigned to the German specialists. 25X1

3. The Soviet chemists were not equal in training to the Germans. They were unacquainted with many chemical processes and conspicuously lacking in the ability to perform chemical calculations. In general they were docile and eager to learn but were distracted from their duties by competitions and political indoctrination. They were especially reluctant to assume responsibility and worked

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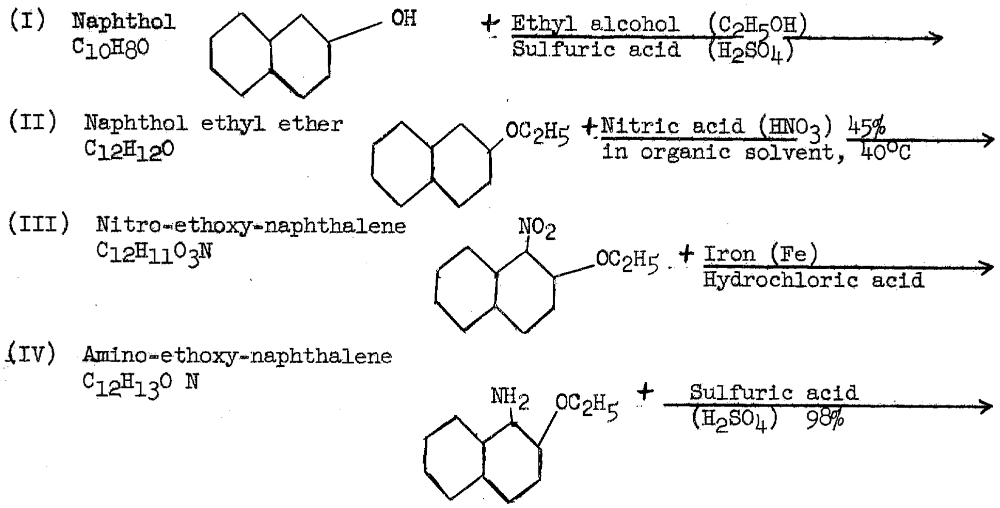
Washington Distribution Indicated By "X"; Field Distribution By "#". [redacted] 25X1 only when given positive orders by supervisors. The women assistant chemists were very diligent and were constantly instructed by chemists in both chemical and political subjects. Chemists, as well as assistant chemists, were organized according to work and salary grades; they could be promoted or demoted to higher or lower grades.

25X1 4. [redacted] twenty-three deported German specialists, twenty-one from the Wolfen Farbenfabrik and two from the Deutsche Hydrierwerke in Rodleben arrived at Rubezhnoye. With the exception of one physicist and two engineers all were chemists. Only three of them were employed in their proper field; the others had to familiarize themselves with new subjects. Their duties were made known to them by Professor Voroshtsov (fnu), director of a Moscow scientific dye stuff laboratory, who determined the possibilities of employment and the salary for each member of the German team. Salaries were between 4,000 and 7,000 rubles. After reading scientific literature for one month, the Germans were assigned a temporary laboratory with small and simply-equipped rooms. The supply of current and gas was irregular. The gas, which was a benzol-air mixture, was so irregularly supplied that the burners often went out and benzol vapor appeared in the rooms. This was extremely detrimental to the health of the working staff in the laboratory and affected the hemoglobin level of the blood, decreasing it from 90 to 70 percent. The glass equipment was very poor and tins and glasses for conserves were used to a very large extent. From time to time glass equipment delivered as reparations, or resulting from dismantlings, arrived from Germany but most of it was stolen before reaching the laboratory. Writing paper was scarce, too, and packing paper was generally used for writing. In mid-1947, the German team moved into a new laboratory with better equipment which had been constructed for them. The installations were not perfect but the laboratory ensured undisturbed work to a certain degree. A library on the fifth story of the building became useful gradually. All major chemical works had been seized in Germany.

5. A so-called <u>tekhnikum</u>, an experimental plant where all major experiments of the processes developed in the laboratory were executed under commercial conditions, was attached to the laboratory. Although equipped with modern instruments from Germany and Hungary, the tekhnikum lacked implements and tools. It was directed by Popov (fnu), a Soviet chemist who was assisted by five other Soviet chemists. They worked in three shifts, and the German specialists had only to express their wishes on the technique of the processes to control the experiments. They were never informed whether the processes were adopted for regular production nor were they allowed to enter the production shops.

Industrial Research on Dyestuffs and Dyestuff Intermediates.

6. Ethoxy-Cleve acid, intermediate product for dyestuff.



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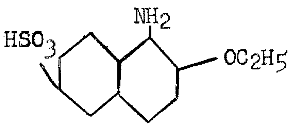
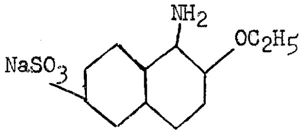
(V) Amino -ethoxy-naphthalene-sulfonic acid $C_{12}H_{13}O_4SN$



$+ \xrightarrow[\text{(NaCl)}]{\text{Sodium chloride}}$

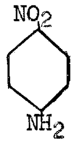
(VI) 1-amino-2-ethoxy-6-naphthalene-sulfonic acid sodium salt
$C_{12}H_{12}O_4SNNa$



The etherification (I), in the Soviet Union, is allegedly supposed to be performed with boric acid (HBO_3) as a catalyst. An orientation experiment failed and was not repeated. The nitration (II) proceeds smoothly. It results, also, in the formation of other nitro compounds which, in the main, remain in solution, while the 1-nitro compound precipitates. The 1-nitro-2-ethoxy-naphthalene (III), which has been filtered off and dried, is sufficiently pure for further treatment. The reduction to the amino compound (IV) with iron powder is difficult and tedious. The amino compound so obtained will be distilled in a vacuum, then dissolved in and recrystallized from ethyl alcohol, (C_2H_5OH). Sulfonating (IV) with 98% sulfuric acid and salting out with sodium chloride offer no obstacles at all.

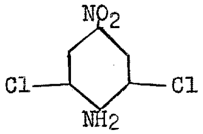
7. Dichloro-nitro-aniline, intermediate product for dyestuff.

(I) Nitro-aniline
$C_6H_6O_2N_2$



$+ \xrightarrow[\text{in hydrochloric acid (HCl)}]{\text{Chlorine } (Cl_2)}$

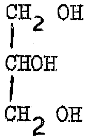
(II) 2,6-dichloro-p-nitro aniline
$C_6H_4Cl_2O_2N_2$



Chlorination with gaseous chlorine is to be preferred, by far, to that of a chlorate ($KClO_3$ or $NaClO_3$). Any excess of chlorine must be avoided, since quinone-like$\left(OC\begin{smallmatrix}CH:CH\\CH:CH\end{smallmatrix}CO\right)$ compounds form immediately and, in addition, the yield promptly drops off. As long as p-nitro-aniline-chlorine hydrate is still present, a test by the spot method on paper containing lignin brings out a blood-red coloration, which is an excellent test for the completion of the reaction. By dissolving it in, and then crystallizing it from concentrated sulfuric acid (H_2HO_4), or by dissolving it in, and then recrystallizing it from methanol (CH_3OH), the product can be purified.

8. Allyl mustard oil, for use on the film area.

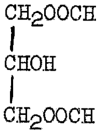
(I) Glycerol
($C_3H_8O_3$)



$$\begin{array}{l}CH_2\,OH\\ |\\ CHOH\\ |\\ CH_2\,OH\end{array}$$

$+ \xrightarrow[\text{HOOCH (86\%)}]{\text{formic acid}}$

(II) Glycerol diformate
($C_5H_8O_5$)



$$\begin{array}{l}CH_2OOCH\\ |\\ CHOH\\ |\\ CH_2OOCH\end{array}$$

$+ \xrightarrow[\text{pyrolysis according to Sandmeyer}]{\text{cuprous chloride (CuCl)}}$

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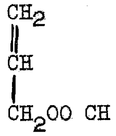
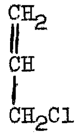
(III) Allyl formate ($C_4H_6O_2$)



$CH_2{=}CH{-}CH_2OO\,CH$

+ $\xrightarrow[\text{concd., up to }50^{\circ}\text{C}]{\text{hydrochloric acid (HCl)}}$

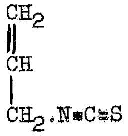
(IV) Allyl chloride (C_3H_5Cl)



$CH_2{=}CH{-}CH_2Cl$

+ $\xrightarrow[(NH_4CNS)\ \text{(rearrangement)}]{\text{ammonium thiocyanate}}$

(V) Allyl mustard oil (C_4H_5NS)

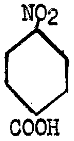


$CH_2{=}CH{-}CH_2.N{=}C{=}S$

The water formed as the result of esterification with formic acid is gradually distilled off in a vacuum; the glycerol diformate, after that, is not further purified. The pyrolysis (III) takes place between 180° and 200°, and must be run very slowly, since completing it too quickly results in other cleavage products. In conversion to allyl chloride (III), one must take into consideration that with hydrochloric acid weaker than 30 percent, the yield drops off rapidly. The final transition to mustard oil is accomplished most readily with ammonium thiocyanate (IV), less readily with potassium thiocyanate (KCNS), and least readily with sodium thiocyanate (NaCNS).

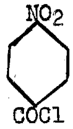
9. <u>p-Nitro-benzoyl chloride, parazol G, parazol G-acid</u>, intermediates for the yellow components of color film.

(I) Nitro-benzoic acid ($C_7H_5O_4N$)



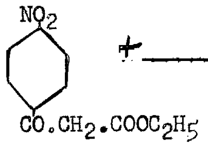
+ $\xrightarrow[\text{phosphorus pentachloride }(PCl_5)]{\text{thionyl chloride }(SOCl_2)\text{ or}}$

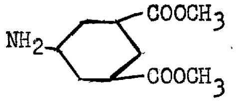
(II) p-nitro-benzoyl chloride ($C_7H_4O\ \ ClN$)



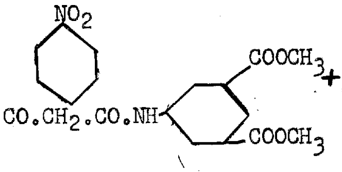
+ $\xrightarrow[C_6H_{11}O_4Na)]{\text{sodium salt of acetoacetic ester}}$

(III) Nitro-benzoyl acetic ester ($C_{11}H_{11}O_5N$)



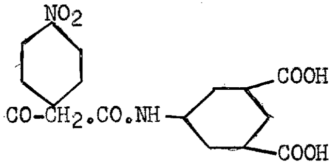
+  $\xrightarrow{\hspace{4em}}$

(IV) Parazol G-ester ($C_{17}H_{10}O_8N$)



+ $\xrightarrow[(KOH)]{\text{potassium hydroxide}}$

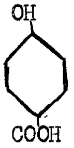
(V) Parazol G-acid ($C_{17}H_{12}O_8N$)



The object of the above work was, on the one hand, to seek reasonably to purify p-Nitro-benzolyl chloride through sublimation, which, however, proved unavailing in respect to the problem of apparatus. Following the instruction of a Soviet expert, the p-nitro-benzoyl chloride in the Soviet Union, was distilled in a vacuum; this, however, did not prove safe. In addition, the difficult condensation with acetoacetic ester was thoroughly studied, and it was found that the success, aside from the pH value (hydrogen ion concentration), is solely dependent on the purity of the nitro-benzoyl chloride. Also, by means of the following stage of operation, in itself easily pursued, and through the introduction of a very pure p-nitro-benzoyl chloride, the yield can be considerably increased. The final stage: the condensation of parazol G-acid, by means of stearyl chloride, to the finished yellow component, could not be accomplished, since a sufficiently pure stearic acid $[CH_3.(CH_2)_{16}.CO_2H.]$ was not available.

10. p-Methoxy benzoyl acetic ester, intermediate for a yellow component of color film.

(I) Hydroxy benzoic acid (Oxy-benzoic acid) $(C_7H_6O_3)$



$+ \xrightarrow[\text{and potassium hydroxide (KOH)}]{\text{dimethyl sulfate } [(CH_3.O)_2SO_3]}$ (1)

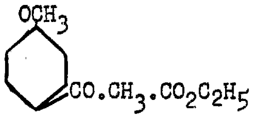
(II) Methoxy-benzoic acid $(C_8H_8O_3)$

$+ \xrightarrow[(PCl_3)]{\text{phosphorus trichloride}}$

(III) Methoxy benzoyl chloride $(C_8H_7ClO_2)$

$+ \xrightarrow[(C_6H_{11}O_4Na)]{\text{sodioacetoacetic ester}}$

(IV) p-Methoxy benzoyl acetic ester $(C_{12}H_{15}O_4)$

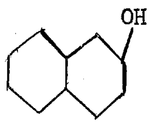


(2)

Here the problem, above all, is to find a method of determination for p-methoxy benzoyl acetic ester (IV). A method was worked out by coupling the ester with diazo solution (sodium nitrite, $NaNO$ + hydrochloric acid, HCl). This work was superseded, because in the meantime, in Moscow, a polarographic method of determination was discovered. However, p-methoxy benzoyl acetic ester, which hitherto had been known only as a liquid, could by this experiment be prepared in a crystallized form for the first time. The pure ester has a fine hawthorn aroma.

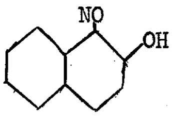
11. Eriochrome blue-black B, azo dye, is processed on a dye for cellulose ester, (nitrocellulose lacquer).

(I) Naphthol $(C_{10}H_8O)$



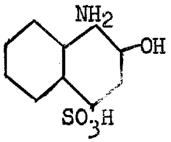
$+ \xrightarrow[\text{sulfuric acid } (H_2SO_4)]{\text{sodium nitrite } (NaNO_2)}$

(II) Nitroso naphthol $(C_{10}H_7O_2N)$



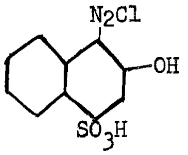
$+ \xrightarrow[\text{sulfuric acid } (H_2SO_4)]{\text{sodium bisulfite } (NaHSO_3)}$

(III) Amidol acid $(C_{10}H_9O_4SN)$



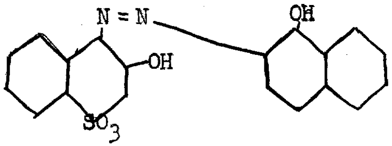
$+ \xrightarrow[\text{hydrochloric acid (HCl)}]{\text{sodium nitrite } (NaNO_2)}$

(IV) $C_{10}H_7O_4ClSN_2$



$+ \xrightarrow[\text{(alkaline)}]{\alpha\text{ naphthol } (C_{10}H_8O)}$

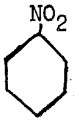
(V) Eriochrome blue-black B
($C_{20}H_{14}O_5SN_2$)



The introduction of the nitroso group (I) poses no difficulties. In the same manner, the reduction and sulfonation (II) performed in a single operation gave little trouble. Contrary to the data of FIERZ-DAVID, the maximum yield amounts to 78-80 percent of the theoretical. The diazotized amidol acid (IV) couples with α naphthol, in a caustic alkaline solution (potassium hydroxide /KOH/ or sodium hydroxide /NaOH/) to form eriochrome blue-black.

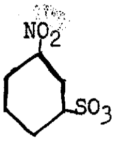
12. Metanil yellow, indicator dye.

(I) Nitro-benzene
($C_6H_5O_2N$)



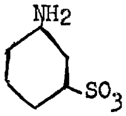
$+ \xrightarrow{\text{Fuming sulfuric acid } (H_2SO_4)}$

(II) Nitro-benzene sulfonic acid
($C_6H_5O_5SN$)



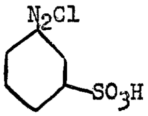
$+ \xrightarrow[\text{Sulfuric acid } (H_2SO_4)]{\text{Iron (Fe)}}$

(III) Aniline sulfonic acid
($C_6H_7O_3SN$)



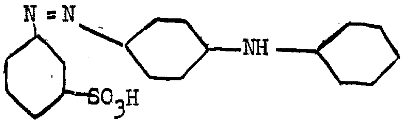
$+ \xrightarrow[\text{Hydrochloric acid (HCl)}]{\text{Sodium nitrite } (NaNO_2)}$

(IV) Diazochlorsulfonic acid
($C_6H_5O_3ClSN_2$)



$+ \xrightarrow[\text{Ethyl alcohol } (C_2H_5.OH)]{\text{Diphenyl amine } (C_6H_5)_2NH}$

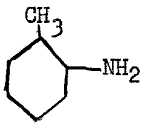
(V) Metanil yellow
($C_{18}H_{14}O_3SN$)



The sulfonation (I) and reduction (II) proceed smoothly. The coupling with diphenyl amine (IV) was undertaken in an ethyl alcohol solution. In methyl alcohol (CH_3OH), duller dyes are formed.

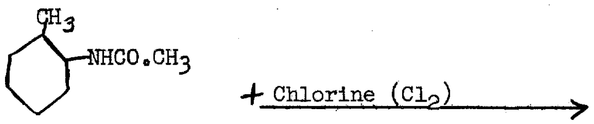
13. Indanthrene red violet RH, vat dye of the thioindigo series.

(I) o-Toluidine
(C_7H_9N)

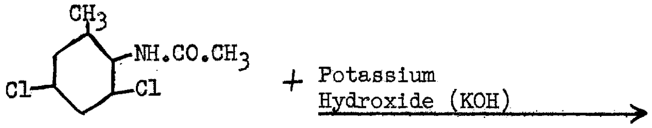


$+ \xrightarrow[\text{or Formic acid } (HCO_2H)]{\text{Acetic anhydride } /(CH_3.CO)_2O/}$

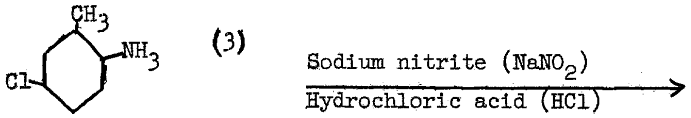
(II) Acet-o-toluidide
($C_9H_{11}ON$)



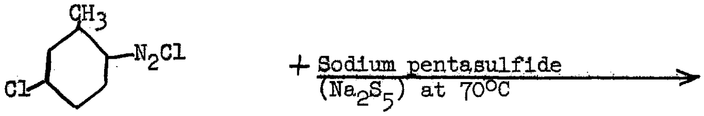
(III) Dichloro aceto-o-toluidide
($C_9H_9OCl_2N$)



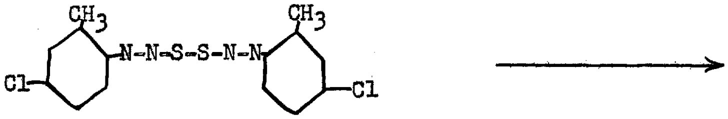
(IV) Chloro amino toluene
(C_7H_9ClN)



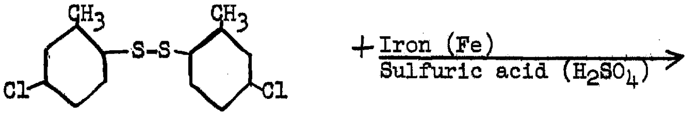
(V) Diazodichloro amino toluene
($C_7H_6Cl_2N_2$)



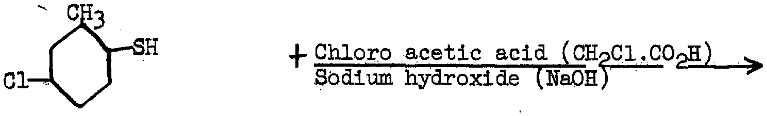
(VI) $C_{14}H_{12}Cl_2S_2N_4$



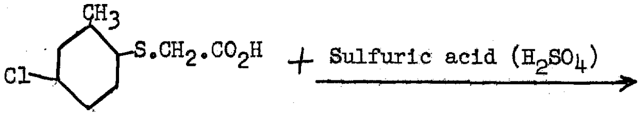
(V) $C_{14}H_{12}Cl_2S_2$



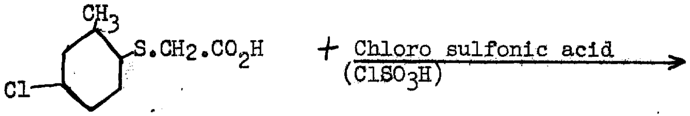
(VI) C_7H_6ClS



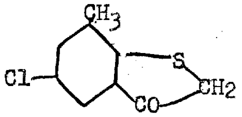
(VII) $C_9H_9ClO_2S$



(VIII) Thio- 3B - acid
($C_9H_9ClO_2S$)

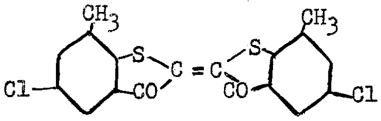


(IX) Thionaphthene chloride
(C_9H_7ClOS)



$+$ Bromine (Br) $\longrightarrow$

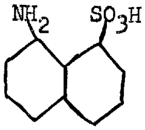
(X) Indanthrene red violet RH
($C_{18}H_{14}Cl_2O_2S_2$)



First, following the old process of I.G.Farben, the o-toluidine (I) was subjected to acetylation. The diacetyl compound is chlorinated (II) in an aqueous suspension and saponified under pressure with sodium hydroxide (NaOH) or potassium hydroxide (KOH). Besides 5-chloro-2-acetylaminotoluene, 3-chloro-2-acetylaminotoluene is also formed. Both chlorine compounds are separated by distillation, for which, however, very highly effective columns are required. These columns were not available in Rubezhnoye. Instead of products with a minimum freezing point of 26°C, only products with a freezing point of from 16°C to 18°C were obtained in this manner. Further, a method was discovered whereby both chlorine products could be separated by agitating the aqueous solutions of the hydrochlorides with chlorobenzene. In this manner, the more weakly basic 3-chloro-2aminotoluene was almost quantitatively dissolved in the solvent. In the aqueous layer, enriched 5-chloro-2-aminotoluene hydrochloride remains. Later, an operation was performed in accordance with instructions received from Moscow, whose source remained unknown, in compliance with one which produces the formyl compound of o-toluidine in chlorobenzene. The formyl compound does not have to be isolated, but is directly chlorinated in the chlorobenzene solution (C_6H_5Cl) and processed further. The 5-chloro-2-aminotoluene obtained in this manner is of excellent quality. The 3-chloro compound remains in solution in the chlorobenzene, but, for the most part, passes over into chlorinated quinone compounds. The process is more expensive than that of I.G.Farben, and besides the 3-chloro compound is lost. The advantage lies solely in the fact that one can obtain a pure product without any highly effective fractionating apparatus. The diazotization proceeds normally (IV), yet the conversion with sodium pentasulfide (Na_2S_5)(V) presents certain difficulties. The Na_2S_5 solution is applied at 70°C, and the diazo solution is permitted slowly to run into it, in order to assure the immediate decomposition of the explosive diazodisulfide compound. Since the diazo solution itself is quite readily decomposed, care should be taken at the influx that the solution itself does not become warm before it has reached the reaction mass. This stage of the operation, at one beginning point of the process, might present the greatest difficulty. The reduction (V) and the glycination (VI) present no obstacles. The thio-3-B-acid (VIII) is isolated and dried. The thionaphthene compound (IX) forms quickly through the action of the chloro sulfonic acid on the thio-3B-acid (VIII). In order to obtain a dye which conforms to standard, the chloro sulfonic acid employed must be especially pure, particularly in regard to a content of oxidizing substances, otherwise the dyes will take on a blue tinge. This dye was stricken from the production program of the Rubezhnoye combine, since a sufficiently pure chloro sulfonic acid was not available.

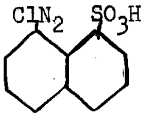
14. Vat printing black BL, vat dye.

(I) Naphthylamine sulfonic acid
($C_{10}H_9O_3SN$)



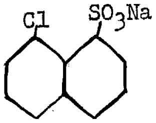
$+ \frac{\text{Sodium nitrite } (NaNO_2)}{\text{Hydrochloric acid } (HCl)}$

(II) Chloro naphthalene sulfonic acid ($C_{10}H_7ClO_3N_2S$)



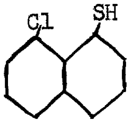
+ $\xrightarrow[\text{Sodium chloride (NaCl)}]{\text{Cuprous chloride (CuCl)}}$

(III) Chloro naphthalene sodium sulfo acid ($C_{10}H_6ClO_3SNa$)



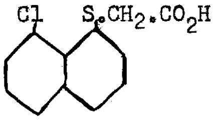
+ $\xrightarrow[\text{Sulfuric acid } (H_2SO_4)]{\text{Zinc dust (Zn)}}$

(IV) Chloro naphthalene sulfide ($C_{10}H_7ClS$)



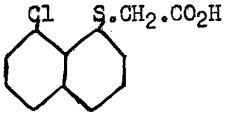
+ $\xrightarrow[\text{Potassium Hydroxide (KOH)}]{\text{Chloro acetic acid } (CH_2ClCOOH)}$

(V) Chloro naphthalene thio-glycolic acid ($C_{12}H_9ClO_2S$)



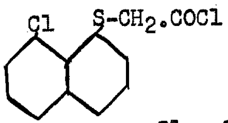
+ $\xrightarrow[(H_2SO_4)]{\text{Sulfuric acid}}$

(VI) The same as (V)



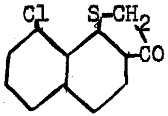
+ $\xrightarrow[(PCl_3)]{\text{Phosphorus trichloride}}$

(VII) $C_{12}H_8Cl_2OS$

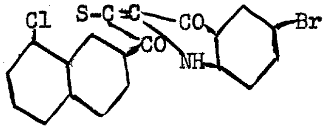


$\longrightarrow$

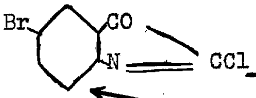
(VIII) $C_{12}H_7ClOS$



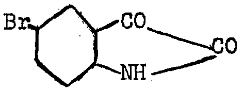
(XII) Indanthrene printing black ($C_{20}H_9BrClO_2SN$)



(XI) Bromoisatin chloride ($C_8H_3BrClON$)

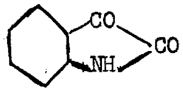


(X) Bromoisatin ($C_8H_4BrO_2N$)



+ Phosphorus pentachloride (PCl_5)

(IX) Isatin ($C_8H_5O_2N$)



+ Bromine (Br_2)

The diazotization (I) and the Sandmeyer reaction (II) present no difficulties. The 8-Chloro naphthalene-1-sulfonic acid sodium salt (III) is isolated. The further processing to 8-chloro naphthalene -1-thioglycolic acid (IV) also offers no obstacles, whereas the condensation of the thionaphthalene compound with bromoisatin chloride (XII) is sensitive. If, in the production of bromoisatin chloride (X), the hydrogen chloride formed is not drawn off and the operation is not immediately carried further, dyes with muddy, dirty shades are formed. The dye was prepared in all stages by a German expert in the technical institution of the combine.

15. Dibromo isoviolanthrone, vat dye.

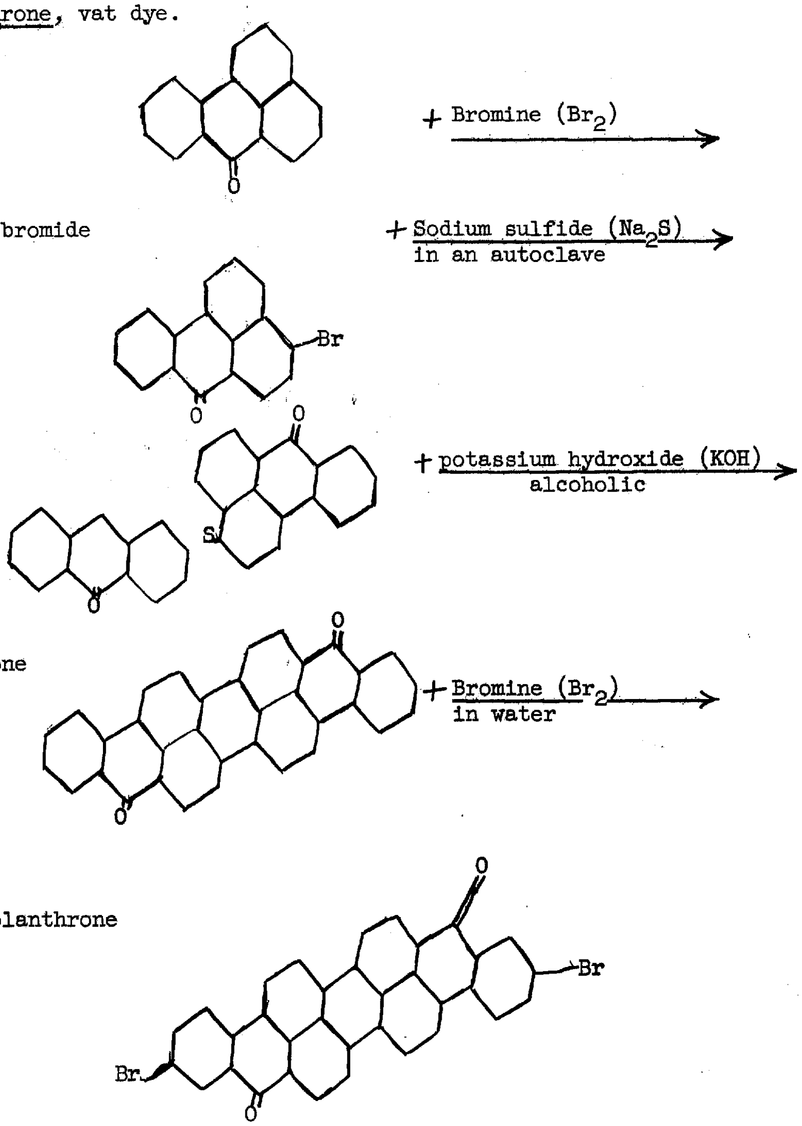
(I) Benzanthrone ($C_{17}H_{10}O$)

(II) Benzanthrone bromide

(III) $C_{31}H_{17}O_2S$

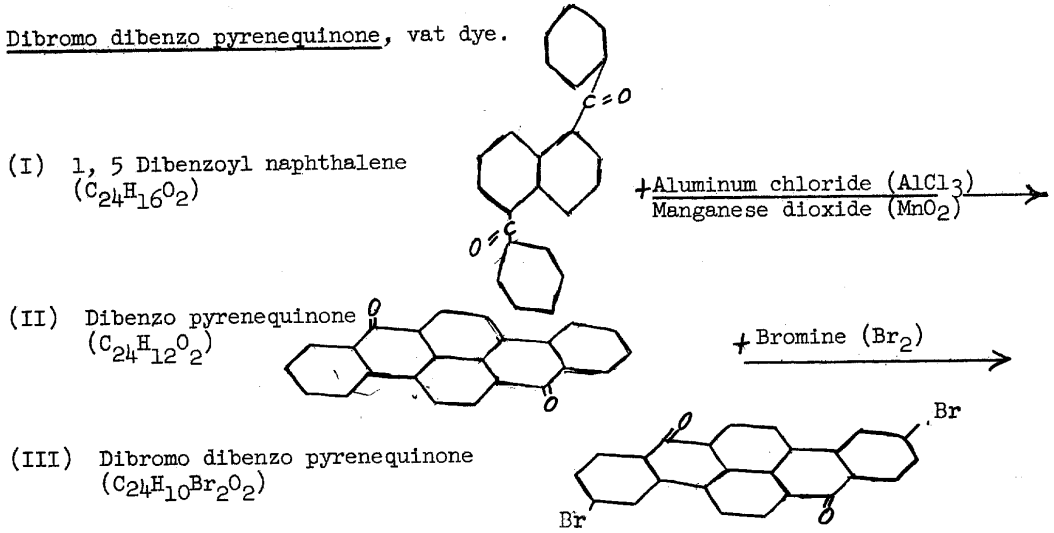
(IV) Isoviolanthrone ($C_{34}H_{16}O_2$)

(V) Dibromo isoviolanthrone ($C_{34}H_{14}Br_2O_2$)



The bromination of benzanthrone (I), sulfidization (II) and desulfurization (III) proceed smoothly. The bromination of isoviolanthrone, following a Soviet patent of Krolik[4], was supposed to take place in an aqueous suspension (IV) at 30°C, and with a quantity of bromine amounting to 600 per cent of the theoretical. This was not the case. All dyes prepared in this manner were too reddish. The German expert discovered that dyes according to type can be obtained at 70°C, with 300 per cent of bromine.

16. Dibromo dibenzo pyrenequinone, vat dye.



(I) 1, 5 Dibenzoyl naphthalene ($C_{24}H_{16}O_2$)

+ Aluminum chloride ($AlCl_3$) / Manganese dioxide (MnO_2) →

(II) Dibenzo pyrenequinone ($C_{24}H_{12}O_2$)

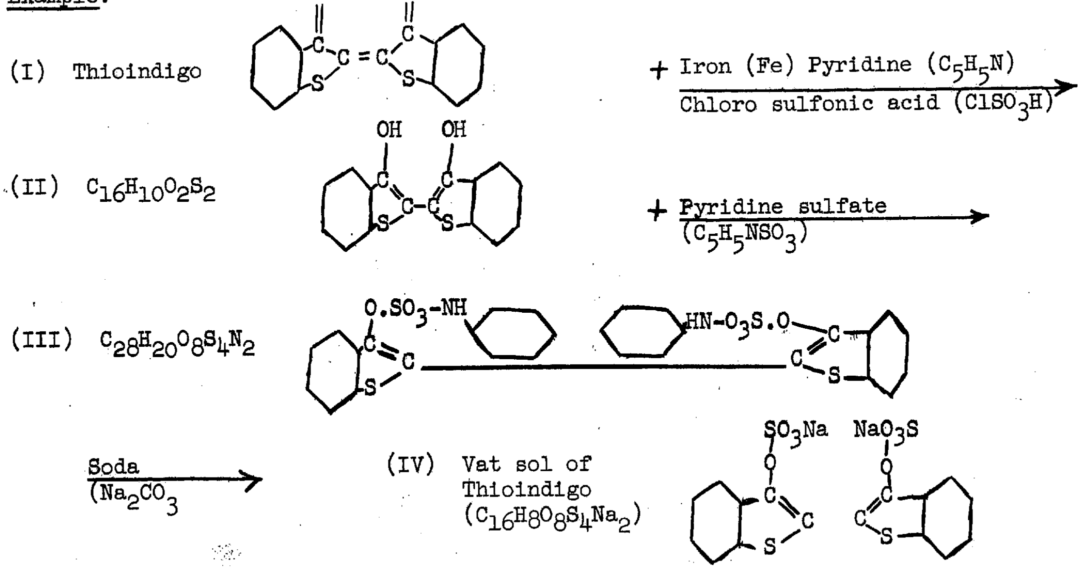
+ Bromine (Br_2) →

(III) Dibromo dibenzo pyrenequinone ($C_{24}H_{10}Br_2O_2$)

The preparation of the dye proceeds without any particular difficulty, with a moderate yield, to be sure. Application of manganese dioxide proved the latter to be absolutely essential as a hydrogen-absorbing substance.

17. Vat sols, ester salts of vat dye compounds.

Example:



(I) Thioindigo

+ Iron (Fe) Pyridine (C_5H_5N) / Chloro sulfonic acid ($ClSO_3H$) →

(II) $C_{16}H_{10}O_2S_2$

+ Pyridine sulfate ($C_5H_5NSO_3$) →

(III) $C_{28}H_{20}O_8S_4N_2$

Soda (Na_2CO_3 →

(IV) Vat sol of Thioindigo ($C_{16}H_8O_8S_4Na_2$)

The quality of the iron used (I) for the reduction of the thioindigo is important for the course of the operation. A special reduction iron is best. The German expert prepared from five to six kg of indigo dyes the appropriate vat sols, i.e. depending on the solubility, either the sodium salt or the potassium salt (III). In one case, which involved a pink dye, the salt of triethanolamine was prepared ($/\overline{\ }CH_2\ \overline{7}_6/\overline{\ }OH\ \overline{7}_3N$). Previously, two to three moles of ethylene oxide $/\overline{(}CH_2)_2O\ \overline{7}$ per ethanol group had been added to the base. This vat sol was a syrup-like, brown liquid, whereas all the other were in the form of white or weakly-colored crystals.

25X1 [redacted] Comments

1. This formula should be written $[(CH_3)_2SO_4]$.
2. This formula should be written $CO.CH_2.CO_2C_2H_5$.
3. This formula should be written NH_2.
4. Very likely this is the Soviet scientist L. Krolik who is known for his work in organic chemistry.