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THE CHEMICAL COMPOSITIONS OF GERMAN PYROTECHNIC SMOKE SIGNALS

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COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE

LONDON—H.M. STATIONERY OFFICE

THE CHEMICAL COMPOSITIONS OF
GERMAN PYROTECHNIC SMOKE SIGNALS

Report by:

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G-2 Division, SHAEF (Rear) APO 887

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THE CHEMICAL COMPOSITIONS OF GERMAN PYROTECHNIC SMOKE SIGNALS

I. SUMMARY

As a result of the investigation of a number of German pyrotechnic plants, information concerning the chemical compositions of some white, black and colored smoke mixtures has been obtained.

It has been found that the colored smoke compositions were mixtures of organic dyestuffs, potassium chlorate, kieselguhr and lactose, which were granulated by means of water and a water soluble binder. These compositions are given in detail. The chemical formulae of the organic dyestuffs used in these compositions were obtained from the I.G. Farbenindustrie and are given in the appendix of this report.

The white smoke compositions have been found to be either phosphorus phlegmatized with ten percent of paraffin, or mixtures of hexachlorethane with zinc dust.

Two different types of black smoke compositions have been found. The formulae of these compositions are given also.

II. SOURCES OF INFORMATION

A. Interrogation of Dr. Pahlke, formerly of the DEPYFAG (Deutsche Pyrotechnische Fabrik) plant at Malchow near Berlin. Place of interview: Silberhutte/Harz on June 10, 1945.

B. Investigation of the I.G. Farbenindustrie plant at Leverkusen on 13 August 1945. Person interviewed: Dr. Beck.

C. Investigation of the I.G. Farbenindustrie plant at Hochst on 8 October 1945. Person interviewed: Dr. Huss.

D. Investigation of the I.G. Farbenindustrie plant at Ludwigshafen on 5 October 1945. Person interviewed: Dr. Schimmer.

E. Interrogation of Dr. Fischer, formerly Chief of Development Section, Fabrik Deleu, at Schonhagen/Trebbin. Place of interview: Fabrik Moog at Ronsdorf/Wuppertal on 11 August 1945.

F. Investigation of the Duetsche Pyrotechnische Fabrik (J. F. Eisfeld G.m.b.H.) at Silberhutte/Anhalt during the period 7-12 June 1945. Persons interviewed: Director Schneider & Dr. Kirschener, Chemist.

G. Investigation of the Deutsche Pyrotechnische Fabrik at Kunigunde/Goslar on 12 July 1945. Person interviewed: Mr. Jacob Franzen.

H. Investigation of the Hanbskammer Versuchs Platz near Unterluss on 16 July 1945. Person interviewed: Oberst Hirsch

III. COLORED SMOKE COMPOSITIONS

A. General Introduction:

In Germany, development work on the production of colored smokes to be used as signals during daylight began at the time of the first World War. The first efforts were directed toward the use of colored vapors, e.g. violet iodine vapor, purple manganese fluoride vapor, brown nitrogen dioxide vapor, and green nitrsobenzene vapor (Source A). However, favorable results were not obtained and work in this direction was discontinued. A few experiments were also carried out with the idea of scattering colored dust clouds of inorganic or organic dyestuffs by means of small axial charges of explosive inserted in the containers. Negative results were again obtained, since the volume of smoke produced was far too small when compared with the volume of dyestuff necessary (Source A). This was particularly true of small pistol signals, where only a small space for dyestuff was available.

The first serviceable colored smoke compositions were devised by the Americans, at the end of the first World War. They consisted of mixtures of potassium chlorate, lactose and organic dyestuffs. The organic dyestuffs were vaporized by means of the heat evolved from the combustion of potassium chlorate and lactose. The vapors then condensed in the air to form large clouds consisting of finely divided particles of condensed dyestuff. These smoke signals suffered from the disadvantage (Source A) of using dyestuffs which were not particularly suited to the purpose. The dyes employed, e.g., indigo, paranitroaniline red, chrysoidin, etc., produced dull and impure colors. At distances of a few kilometers it was no longer possible to distinguish blue, red, and yellow colored smokes (Source A).

In order to improve the colors produced by smoke mixtures of this type, the DEPYFAG plant at Malchow carried out an extensive series of tests with new dyestuffs. The new dyes were suggested and furnished by the I.G. Farbenindustrie Research Staff at Ludwigshafen.

Only those dyestuffs which possessed relatively low vaporization temperatures and which were able to resist the process of vaporization without chemical change were tested. Promising results were obtained with dyes of the "Sudan" class. By means of a dye of this type, called "Sudanblau G", the first really usable German blue smoke composition was developed. The formula was as follows:

<u>Blue Smoke Composition</u>

Potassium chlorate	25%
Lactose	25%
Sudanblau G	37.5%
Kieselguhr	12.5%

The chemical formula of Sudanblau G, as well as those of the other dyestuffs mentioned in this report, are given in the appendix.

The Kieselguhr was added to the composition both in order to render it lighter and more porous and also in order to economize in the use of dyestuff (Sudanblau cost approximately thirty marks per kilogram and the replacement of 12.5% of it by means of the inexpensive kieselguhr was considered a very considerable economy) (Source A).

The above composition was used in the "Handrauchzeichen" or "Hand Smoke Signal", which consisted of a cylindrical paper case with a single smoke outlet in the base. The composition was simply tamped by hand into the container.

Green and violet colored smokes were also produced at the same time. Since there were no single green or violet dyes available for the purpose, mixtures of dyes were used. The formulae for the smoke compositions were as follows:

<u>Green Smoke Composition</u>

Potassium chlorate	28%
Lactose	25.0%
Auramine	31.7%
Sudanblau G	12.3%
Kieselguhr	3 %

<u>Violet Smoke Composition</u>

Potassium chlorate	25%
Lactose	22%
Rhodamine	44%
Sudanblau G	6%
Kieselguhr	3%

A very large number of tests were made in order to produce red and yellow smoke generators in an analagous manner, using pressed composition and a single smoke outlet in the signal container. Very poor results were obtained. Using yellow and red dyes of the "Sudan" class, in quantities occasionally as high as 60% of the total weight of composition, it was observed that the color of the smoke was red or yellow at the beginning of the evolution; however, after a short time, the color turned white.

By working in conjunction with the staff of I.G. Farben, it was finally found that the cause of the whitening of the smoke was the catalytic decomposition of the dyestuff vapors due to contact with hot carbonaceous residues (slag) formed by the combustion of the initially burned smoke composition (Source A). In the smoke generator which employed pressed composition with only a single smoke outlet, the vaporized dyestuffs always had to pass hot carbonaceous residues before reaching the open air. The yellow and red dyestuffs were not able to resist this treatment and were catalytically converted to colorless compounds.

Therefore, in order to develop satisfactory red and yellow colored smoke generators, a method of leading the smoke out into the open air without contacting the slag had to be developed. Two methods of accomplishing this task were devised: a) the use of loosely filled, granulated smoke composition, and b) the introduction of "sieve tubes" passing through the smoke generator from top to bottom, connected to the smoke outlets in the tops of the generators.

The first of these,ie. the use of granulated composition, proved to be quite valuable. The process of granulating the smoke composition involved mixing the composition in the presence of water with the addition of small amounts of either methyl cellulose or water glue binders. The compositions were mixed in apparatus which was quite similar to that shown below.

After mixing, the composition while still moist, was passed through an ordinary meat grinder equipped with a disc having holes 4 mm in diameter. The long strands of moist smoke composition obtained in this manner were dried at 30°C. As a result of the drying process, the strands disintegrated into small grains about 4mm in diameter and 8 mm in length. The loading of smoke generators with loose, granulated composition provided a larger volume of free space through which the smoke could pass without contacting the usual amount of hot slag.

It was with the aid of granulated smoke composition that the first successful German red smoke generator was produced. The composition was as follows:

<u>Red Smoke Composition</u>

Potassium chlorate	20%
Lactose	20%
Sudanrot G	55%
Kieselguhr	4%
Methyl cellulose	1%

TALPO.IT
TALPO.IT

MIXING EQUIPMENT

Several difficulties in the manufacture of generators containing this composition were encountered. The first was the very great effect of moisture upon the burning rate. In order to produce generators with a constant and reproducible burning time, it was found necessary to dry the composition very carefully, first at 30°C, and then in heated rooms, for approximately one week, in order to obtain a constant moisture content.

A second difficulty encountered in the production of all types of smoke generators was the inflammability of the colored smoke when it had reached the open air. In certain cases, merely the insertion of a glowing splint into the colored smoke stream sufficed to ignite the smoke and cause a flame which destroyed the color. According to actual measurements, the temperature of the smoke inside the generators ranged from 450° to 700°C. Therefore efforts were made to cool the smoke to some extent before it reached the open air. This was accomplished by means of the metal sieve tubes which were inserted into the granulated smoke composition. These acted in the same way as the well known miners safety lamp, in conducting heat away from the smoke. These sieve tubes also served to provide paths whereby the smoke could reach the open air without coming in contact with the hot slag in the interior of the generators.

Some experiments had also been carried out with ammonium perchlorate as the oxidant in place of potassium chlorate in order to reduce the tendency toward the production of flame (Source A). It was thought that the nitrogen which would be produced as the result of the combustion would act as an inert gas and prevent inflammation. However, it was reported that large quantities of hydrochloric acid were evolved by the reduction of the ammonium perchlorate. The hydrochloric acid together with the high temperature in the chamber caused the destruction of the color of the dyestuff (Source A) and rendered the use of ammonium perchlorate impracticable.

The use of granulated smoke composition in place of pressed composition was found to be useful for the production of other smoke signals with short burning times and high rates of smoke evolution. The large surface area and large burning surface of the granulated composition caused a very high rate of smoke evolution which could not be produced in any other way. Indeed, efforts to produce fast burning colored smoke compositions by means of increases in the potassium chlorate content had been tried, but were unsuccessful. Whenever the amount of potassium chlorate was increased to more than 35%, the color of the smoke became gray. This was found to be true for all colors (Source A) and was thought to be due to oxidation of the dyestuff by the increased quantities of potassium chlorate. This was further explained by the fact that all colored smoke compositions must contain a rather large excess of dyestuff. For example, red smoke compositions were said to become unusable when the content of dyestuff fell below 45%. Blue compositions were less sensitive, due to the great coloring strength of Sudanblau G; however, if the content of dyestuff fell below 35%, the color was said to become very weak also.

From the above discussion, it is apparent that the use of granulated composition was very important in the production of colored smoke generators, particularly those having a high rate of smoke evolution. A typical example of its usefulness was the development of a smoke generator containing 200 grams of composition in a volume of about 350 cc, having a burning time of from 2-5 seconds. This was said to have been impossible using ordinary pressed composition.

Some disadvantages which resulted from the use of granulated smoke composition were a) the rather long and involved manufacturing procedures and b) the fact that the amount of granulated smoke composition which could be placed in a given volume was not as large as the amount of pressed composition which could be inserted in the same volume.

For some types of smoke signals, the use of tableted, pressed composition was found to be more advantageous. The tablets were pressed in automatic tableting presses, and were formed as large cylinders whose outer diameters were equal to the inner diameters of the signal containers. The tablets usually possessed axial holes through which the sieve tubes of the smoke generators could pass.

The tableted compositions were quite similar to the usual compositions, and differed only in that talcum was used in place of kieselguhr. The talcum facilitated the pressing of the composition in the tableting presses.

In the last year of the war, the lactose necessary for the manufacture of smoke compositions became critical, and was therefore replaced partially by woodmeal. A typical composition employing woodmeal together with talcum is the following:

Tableted Orange Smoke Composition
Used for Rauchsichtzeichen Orange 80

Potassium chlorate	29%
Lactose	13%
Woodmeal	5%
Orange 1584	27%
Talcum	10%
Rauchorange	16%

Most of the violet smoke compositions contained Rhodamine B, which was rather strongly acid, and possessed a pH of approximately 2. Considerable anxiety was expressed concerning the use of this dyestuff in compositions containing potassium chlorate. A large number of tests were therefore carried out with a view toward the development of chlorate-free smoke compositions. At first, efforts were made to replace the potassium chlorate with ammonium perchlorate, then with potassium perchlorate, and finally with nitrates.

No detailed results of the effect of the substitution of ammonium perchlorate are available. However, it was stated (Source A) that the color of the smoke was either gray or white when ammonium perchlorate was employed, and it was supposed that the hydrochloric acid liberated by the ammonium perchlorate caused the decomposition of the dyestuff.

Compositions containing potassium perchlorate in place of potassium chlorate were unsuccessful because of greatly decreased ignitability, and also because there was not a sufficiently large variation in burning rate with changes in the composition (Source A). Compositions containing potassium nitrate exhibited the same faults as those containing potassium perchlorate, but to an even greater extent.

Mixtures of dyestuffs with black powder were also tried. It was thought that the black powder would behave in the same way as mixtures of potassium chlorate and lactose, and merely supply heat for the volatilization of the dye. However, it was found that the colored smokes obtained from mixtures of black powder and dyestuffs were always impure and not uniform in color.

Further efforts to develop chlorate-free smoke compositions were therefore discontinued.

In order to avoid the danger of self ignition of violet colored smoke compositions containing both potassium chlorate and the acidic Rhodamine B, the Rhodamine B was replaced by the weakly alkaline dyestuff, Rhodamine Base B Extra. However, the color of the violet smoke obtained as a result of the substitution was not as good as that produced by the original composition. It was stated (Source A) that tests to find a satisfactory dyestuff or mixture of dyestuffs for a violet smoke composition were still in progress, and had not been completed.

It was also stated (Source E) that yellow smoke compositions consisting of potassium chlorate, lactose, and auramine caused a considerable amount of difficulty due to heat evolution and self-ignition in the presence of moisture. The reason for this was not known definitely; but it was thought to be due to an initial reaction between auramine and lactose. It was reported (Source E) that the difficulty was eliminated by mixing the required amounts of lactose and auramine in the absence of potassium chlorate, and then storing this preliminary mixture for a period of approximately one week in order to allow the reaction to complete itself.

Yellow Smoke Puff Composition

This is an interesting example of a fast burning inorganic smoke composition. The composition was as follows:

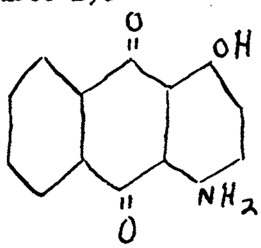
Cadmium metal	19.3%
Cadmium sulfide	20.1%
Zirconium	16.5%
Aluminum	4.0%
Barium nitrate	28.8%
Potassium perchlorate	7.3%
Synthetic resin	4.0%

MOLD USED TO PRESS CYLINDRICAL BLOCKS
OF SMOKE COMPOSITION FOR NEBELKERZEN 39B

MOLD INSIDE PRESS SHOWING LATERALLY
SLIDING BLOCKS (M, N, O) WHICH MAY BE
SLID INTO POSITION OVER OPENINGS IN MOLD

Rauchbordeau BN

This dyestuff was an anthraquinone derivative having the following formula (Source B):



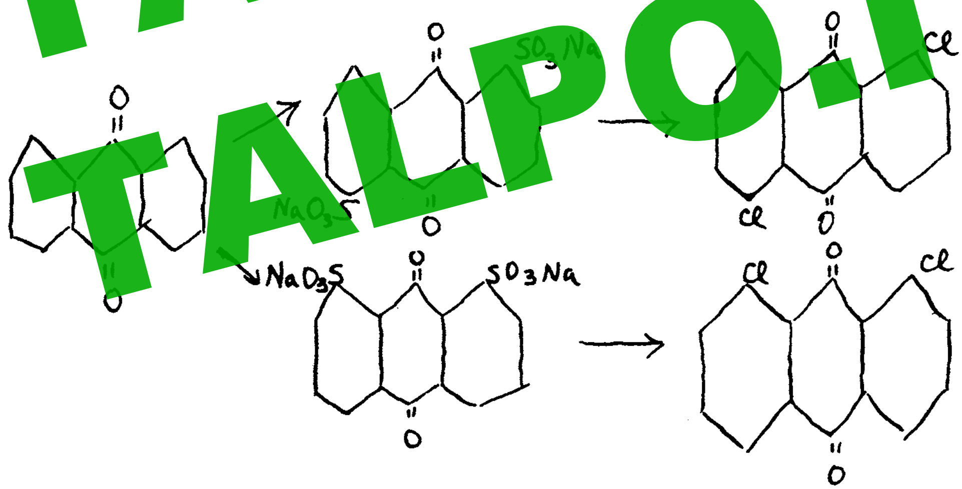
RAUCHBORDEAU "BN"

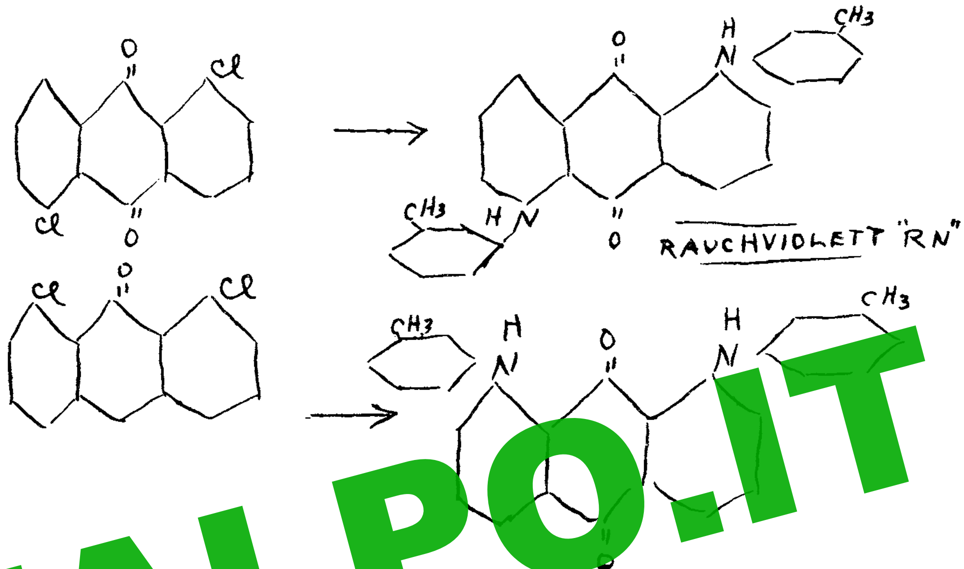
RHODAMINE B
AURAMINE
RHODAMINE BASE B EXTRA
LITHOL ECHT GELB
PARATONER B

These are all well known dyes whose structures are to be found in the standard treatises dealing with dyestuffs.

Rauchviolett RN

This dyestuff was a mixture of two substances which were prepared from anthraquinone by the following reactions (Source B):

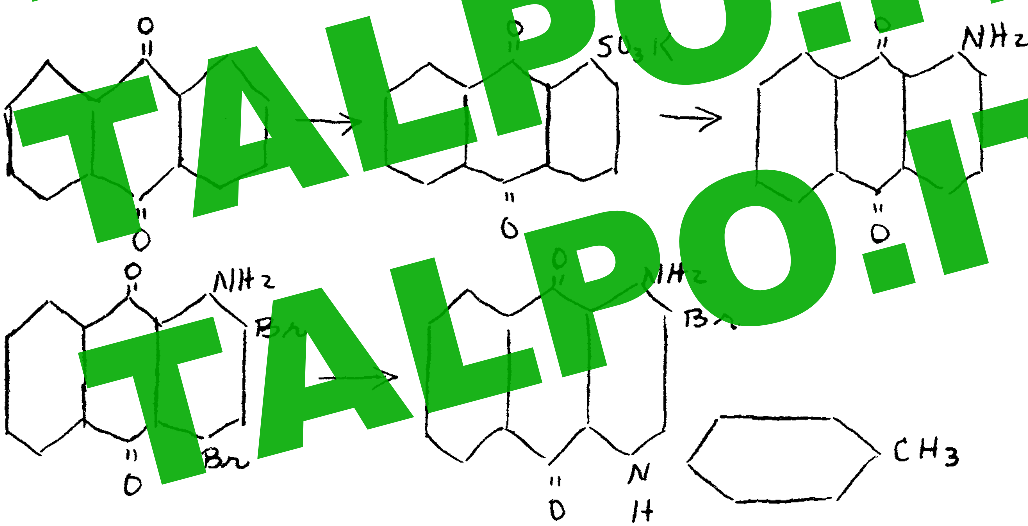




RAUCHVIOLETT "RN"

Rauchblau R

This substance was produced only experimentally. The total quantity which was manufactured was only one hundred kilograms. The synthesis of the dye from anthraquinone was as follows. (Source B):



RAUCHBLAU "R"