Final Report

A SEARCH FOR NEW FUEL COMPONENTS IN EXPLOSIVE MIXTURES WITH AMMONIUM NITRATE

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A search for new fuel components in explosive mixtures with ammonium nitrate.

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by

M.C. Neveu

ABSTRACT

A series of about 80 dye samples was tested by differential scanning calorimetry (DSC) for eutectic formation with ammonium nitrate and release of energy. Thirteen of these showed these desired characteristics. These were in the class of oxazines and dioxazines with ionic groups; and of ionic and non-ionic aminoanthraquinones. A discussion is given about the possibility of the non-ionic aminoanthraquinones to form eutectic mixtures with ammonium nitrate. A synthesis of 2,2',4',6,6',6'-hexanitro-3,3'-biphenol was carried out and its thermal properties as well as those of its potassium and ammonium salts were determined by differential scanning calorimetry. The significance of the use of dyes as fuels in fuel/oxidizer explosive systems and of the use of the Colour Index for the discovery of further intermolecularly reacting explosive systems is discussed.
ACKNOWLEDGEMENTS

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I. INTRODUCTION

It has been well demonstrated in recent and current research that chemical compounds can be chosen, or designed and synthesized, to produce nonideal explosives - particularly intermolecularly reacting ones - which have very attractive characteristics. The characteristics include performance, sensitivity, safety, low cost, industrial availability, strategic and tactical invulnerability, producibility, and mechanical properties.

This has been shown with three totally different systems:

1. nitrate oxidizers and organic fuels (ethylenediamine dinitrate (EDD)/ammonium nitrate (AN), for example;
2. systems in which a compound is specifically synthesized to form a eutectic around the ammonium moiety rather than the nitrate, and which behave almost ideally;
3. high-energy, high density inorganic fuel/oxidizer systems of hydrides and perchlorates.

The systems listed above are two-component intermolecularly reacting ones. One of the factors which governs their effectiveness as explosives is the particle size of the two components; the smaller the particle size, the larger the surface area available for each component to react with one another. This thrust towards smallest particle size leads logically to a search for systems whose components form solid solutions or eutectic mixtures where the particle size is essentially at the molecular size level. The effectively small particle size and high intimacy of the mixed compounds are expected to lead to enhanced performance of potential intermolecular explosives.
II. OBJECTIVES

One of the characteristics of a eutectic mixture is that of a lower melting point than either of its constituent components. The observation of a melting point depression in an approximately equimolar fuel/oxidizer mixture would indicate the formation of a eutectic. It was decided to screen a series of about 80 commercial dyes by Differential Scanning Calorimetry for eutectic mixture formation with ammonium nitrate as evidenced by an endothermic peak below the melting point of ammonium nitrate (169.6°C).

It was expected that certain functional groups in these dyes such as nitro, azo, phenolic, and amino, for example, might contribute to the explosive properties and/or facilitate the formation of eutectic mixtures with ammonium nitrate. Another attractive feature in the choice of dyes as potential fuel components in intermolecularly reacting explosives mixtures with ammonium nitrate is the high industrial production capacity of this country for the manufacture of a great variety of dyes, measured in terms of barrels and tons rather than grams in the case of specialty compounds prepared and synthesized on a laboratory bench scale. In addition, molecular structures, commercial sources, and methods of synthesis for all known dyes are tabulated in an extensive compilation entitled \textit{Colour Index}\textsuperscript{2} In this compilation, dyes are assigned a given Colour Index (C.I.) Number. In this arrangement, dyes with a specific major structural feature are enclosed within a given C.I. No. range (i.e. monoazo dyes 11000-19999; disazo dyes 20000-29999; xanthene dyes 45000-45999; anthraquinone dyes 58000-72999 etc.). Finding of explosive properties and eutectic mixture formation for a
particular dye would suggest that other dyes within the same C.I. No. classification system would show similar behavior. Thus, the classification system might be useful in the selection of other dyes with desirable properties. Indeed, because of molecular structure differences within a given C.I. No. range, differences in explosive characteristics among the members would be expected. A wide spectrum of explosive properties might be able to be formulated with fuels selected from a given C.I. No. range or from a variety of such ranges. The ultimate aim stemming from this concept would be the ability to "custom-tailor" an explosive with a specific explosive property profile by selection of an appropriate dye as organic fuel to be mixed with ammonium nitrate or other oxidizer. The immediate goal of this research project is the verification of the hypothesis that members of the same C.I. No. range will have similar behavioral characteristics and to generate initial data base upon which wide-spectrum formulation and "custom-tailoring" would eventually be founded.

Another phase of this research project was the preparation of a highly nitrated molecule, 2,2',4,4',6,6'-hexanitro-3,3'-biphenol and the investigation of its properties as well as those of its salts as potential explosives.

![Diagram of the molecule](image)

Figure 1. 2,2',4,4',6,6'-hexanitro-3,3'-biphenol
III. FORMATION OF EUTECTIC MIXTURES BETWEEN DYES AND AMMONIUM NITRATE

Mixtures of dye and ammonium nitrate about 50% by weight in each component were studied with a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1B. The DSC scans were carried out in two sweeps: the first from the temperature at which the DSC came under temperature control, 57°C, to 177°C - somewhat above the melting point of ammonium nitrate. This assured proper mixing of the two components. The second sweep was started, again, at 57°C and was carried on through any exotherm that followed.

Experiments which did not result in formation of eutectic mixtures usually showed identical DSC thermograms, specifically, two endotherms; one occurring at 127°C involving a phase transition for ammonium nitrate; the other at 170°C for the melting of ammonium nitrate. Experiments which did lead to eutectic mixture formation usually showed a disappearance or diminution of the 170°C melting of ammonium nitrate endotherm and the appearance of a new endotherm corresponding to the melting of the eutectic. This new endotherm was centered at 112°C (standard deviation 6.6°C) for the thirteen dyes showing eutectic mixture formation. The exotherm which followed was generally sharp and strong with a half-peak width between 20°C and 40°C. In several cases, the pen of the recorder went off-scale indicating the liberation of a great deal of energy. For the same set of dyes, the exotherm was centered at 235°C (standard deviation: 13.0°C).

Table I gives the DSC data for the dyes which formed eutectic mixtures. A copy of the Colour Index entry for all the dyes tested is given in Appendix A. A considerable number of samples tested have the same C.I. No. These entries include C.I. No.; commercial and alternative names; molecular structure (pi electrons of benzene rings have been omitted in this compendium); chemical and physical properties;
TABLE I  Temperatures of endotherms and exotherms for eutectic mixtures

<table>
<thead>
<tr>
<th>Colour Index No.</th>
<th>Temperature of endotherm (°C)</th>
<th>Temperature of exotherm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51080</td>
<td>115</td>
<td>249</td>
</tr>
<tr>
<td>51120</td>
<td>129</td>
<td>222</td>
</tr>
<tr>
<td>51300</td>
<td>105</td>
<td>217</td>
</tr>
<tr>
<td>51310</td>
<td>105</td>
<td>230</td>
</tr>
<tr>
<td>56055</td>
<td>111</td>
<td>243</td>
</tr>
<tr>
<td>60710</td>
<td>109</td>
<td>227</td>
</tr>
<tr>
<td>61110</td>
<td>117</td>
<td>253</td>
</tr>
<tr>
<td>61500</td>
<td>109</td>
<td>241</td>
</tr>
<tr>
<td>61505</td>
<td>111</td>
<td>219</td>
</tr>
<tr>
<td>61515</td>
<td>113</td>
<td>249</td>
</tr>
<tr>
<td>61570</td>
<td>107</td>
<td>227</td>
</tr>
<tr>
<td>64500</td>
<td>117</td>
<td>242</td>
</tr>
<tr>
<td>65005</td>
<td>107</td>
<td>249</td>
</tr>
</tbody>
</table>

and lastly, literature and patent references. Lists of manufacturers for specific C.I. numbers can be obtained from other volumes of Colour Index.

Colour Index numbers 12010 through 26150, given in Appendix A, all azo or disazo dyes, gave negative results. It will be noted that these are all non-ionic. Conversion of these into salts (phenolate or ammonium) might result in eutectic formation, and possibility of taking advantage of the functional groups such as nitro and azo groups in their contribution to explosive properties.

Dyes from C.I. No. 51080 through 51319 all gave positive results.
except for C.I. No. 51319. It might be noted that C.I. No. 51319 is non-ionic and the others in this grouping are ionic. These compounds are in the class of oxazines or dioxazines.

The series from C.I. No. 56055 through 65005 consisted of nine successful and four unsuccessful trials. Most of these are substituted anthraquinones with the exception of C.I. No. 56055 which has an analogous structure. The successful anthraquinones (or analogue) all have at least one amino group on a side benzene ring and many have two amino groups (somewhat reminiscent of the prototype eutectic forming fuel, ethylene diamine (as a double nitrate salt EDD, mentioned in the introductory portion of this report)).

Two of these (C.I. No. 61570 and 65005) are already ionic. In the event that ionicity is necessary for eutectic mixture formation, it may be possible that the non-ionic dyes with amino groups reacted with excess ammonium nitrate to form the ammonium nitrate salt of the dye with the concomittant release of ammonia as follows:

\[
Dye-\text{NH}_2 + \text{NH}_3\text{NO}_3 \rightarrow Dye-\text{NH}_3\text{NO}_3 + \text{NH}_3
\]

Studies carried out at the High Explosives Research and Development Facility at Eglin AFB during a two-week visit at that facility between semesters of the 1980-1 academic year pointed to this conclusion.

A program of converting the amino anthraquinones to their corresponding ammonium nitrate salts by neutralization with nitric acid and studying their eutectic forming ability with ammonium nitrate has been initiated in this laboratory.
IV. SYNTHESIS OF 2,2',4,4',6,6'-HEXANITRO-3,3'-BIPHENOL

The synthesis of the title hexanitrobiphenol was carried out by the nitration of 3,3'-biphenol. This latter compound is not commercially available and it was intended to prepare it by a fairly extended synthetic route described by Mascarelli and Visintin. It was, however, discovered that one of the intermediate compounds in this synthetic route, namely 3,3'-dimethoxybiphenyl, was commercially available (Aldrich Chemical Co. Inc.; 940 W. St. Paul Ave.; Milwaukee, Wisconsin 53233). Consequently, the synthesis was considerably shortened to one involving the cleavage of 3,3'-dimethoxybiphenyl (A) to 3,3'-biphenol (B) followed by nitration to 2,2',4,4',6,6'-hexanitro-3,3'-biphenol (C) as shown in Figure II.

Figure II. Reaction scheme for the preparation of 2,2',4,4',6,6'-hexanitro-3,3'-biphenol (C)
In a typical experiment involving the preparation of 3,3'-biphenol (B), 1.27 grams (5.93 millimoles) of 3,3'-dimethoxybiphenyl (A) was refluxed for 70 hours with 11.71 grams of a 47% by weight aqueous solution of hydrogen iodide (43.03 millimoles HI) in a distillation apparatus consisting of a 60 cm Vigreux column equipped with a distilling head capable of total reflux as well as take-off. Methyl iodide was removed periodically as it formed, and collected in the distilling head take-off tube. The reflux mixture was then cooled, and filtered through a sintered glass funnel of fine porosity to yield 0.79 grams (72% of theoretical yield) of 3,3'-biphenol. Recrystallization from benzene afforded white crystals melting at 125.4-126.4°C (literature value: 123°C).

The nitration of the biphenol (B) prepared above was carried out in the following manner. A mixture consisting of 0.20 g (1.08 millimoles) of 3,3'-biphenol and 2.0 ml of 18 M sulfuric acid was heated with stirring at 100°C on a water bath for three hours. The mixture was then cooled to 80°C, and 2.0 ml of 15 M nitric acid (30.0 millimoles HNO₃) was then added to it. A vigorous evolution of brown fumes ensued and yellow crystals formed immediately. Heating was then stopped and the mixture was stirred overnight. The reaction mixture was filtered with a sintered glass funnel (fine); washed with benzene; and dried in a vacuum oven at 45°C for 75 hours to yield 0.32 grams of presumably hexanitrobiphenol (C) (64.4% of theoretical yield) as yellow crystals.

Nuclear magnetic resonance (nmr) spectroscopic studies confirmed that the nitrated product above had structure (C). A multiplet centered at a delta value of 7.0 ppm in the nmr spectrum of 3,3'-biphenol (B) due to the hydrogen atoms on the aromatic rings disappeared in the spectrum of the nitratd product. A new peak, a singlet at a delta
value of 7.75 ppm appeared in the nmr spectrum of the nitrated product, indicating the presence of uncoupled hydrogen atoms at the 5 and 5' positions of the biphenyl system as in structure (C).

The DSC thermogram showed an exothermic peak at 275°C for the hexanitrated product (C). The potassium and ammonium salts of (C) were prepared by exact neutralization with potassium hydroxide and ammonium hydroxide. The potassium salt (orange) showed a melting endotherm at 108°C and an exotherm at 323°C. The ammonium salt (orange) gave an endotherm at 278°C and an exotherm at 303°C.

V. RECOMMENDATIONS

In view of the possibility that eutectic formation of non-ionic anthraquinones having amino groups may have been made possible by their conversion into ionic compounds by a "direct reaction" described by equation (1) on page 6, occurring while the DSC scan was being made, it would be of interest to convert these anthraquinones into nitrate salts by neutralization with nitric acid and isolate them. Their DSC thermograms could then be made and compared to the DSC thermograms of their corresponding non-ionic counterparts to obtain clues concerning the mechanism of their eutectic formation.

Another project that would be worth considering is the conversion of the non-ionic azo and disazo dyes into ionic compounds by the neutralization of the phenolic group with a suitable base to form sodium, potassium, or ammonium salts. Mixtures of these with ammonium nitrate could then be studied with DSC for eutectic formation with the possibility that this class of compounds with their attractive azo and nitro groups could be used in fuel/oxidizer eutectic mixtures.
It would also be of interest to make quantitative measurements on the exotherms obtained in this project. The exotherm could be scaled up to one having an accurately measurable area. With suitable calibration of the instrument with standards of accurately known heat capacities, the heat released during the exothermic stage of the DSC scan can be obtained from the measurement of the area of the exotherm. This quantitative data could then be used to compare the energy output of the systems studied in this work with each other and with other systems for which this data might be available or measurable.

Lastly, it might be well to construct phase diagrams for the systems studied in which melting points of a series of compositions of fuel and oxidizer are measured by DSC. This would verify the eutectic formation and would give the composition of the eutectic mixture. In addition, thermodynamic properties such as enthalpy, entropy, and free energy could be extracted from these.
APPENDIX A. Colour Index entries for dyes tested for eutectic mixture formation with ammonium nitrate

12010  C.I. Solvent Red 3 (Bordeaux)

\[
\text{C}_9\text{H}_6\text{O}_2\text{N}_2\text{OH}
\]

\(\text{p-Phenazidine} \rightarrow \text{1-Naphthol}\)

Discoverers — O. N. Witt and A. Buntrock 1894
Witt & Buntrock, Ber. 27 (1894), 2360
\(\text{FIAT 764} \rightarrow \text{Sudanbrun II}\)

M.p. 168°C (bronze crystals)
Soluble in ethanol, acetone and benzene

12055  C.I. Solvent Yellow 14 (Reddish yellow)

\[
\text{HO}
\]

Aniline \(\rightarrow\) 2-Naphthol

Häser & Breuwar, JACS, 63 (1941), 419; JSDC, 57 (1941), 1151
Cross, JSDC, 61 (1945), 75

The following deal with metal complex derivatives —
Rikka & Hunter, JACS, 63 (1941), 1598
Drew & Landquist, Ibid, (1941), 293
Drew & Fairbairn, Ibid, (1939), 824
Drew & Dunton, Ibid, (1940), 1063

M.p. 134°C
Soluble in ethanol (orange red), acetone and benzene
Insoluble in water.
HCl conc. — magenta red; on dilution — orange yellow ppt.
HCl conc. — red solution on warming, hydrochloride crystallises on cooling (dark green) but on separation and exposure loses hydrogen chloride.

12075  C.I. Pigment Orange 3 (Bright reddish orange)

\[
\text{NO}_2\text{HO}
\]

2,4-Dinitroaniline \(\rightarrow\) 2-Naphthol

Discoverers — C. Liebermann 1883
\(\text{FIAT 764} \rightarrow \text{Sudanorange R}\)
Liebermann, Ber. 16 (1883), 2860
Zincke & Binneweld, JACS, 22 (1929), 3031
Margery, Gaz. 14 (1894), 271
Zincke & Kauflin, Ber. 19 (1886), 2432
Dennex, Gaz. 15 (1885), 405
Zincke & Lawton, Ber. 20 (1887), 2973
Fischer & Wimmer, Ibid, 20 (1887), 1379
Weinberg, Ibid, 20 (1887), 3172
Jacobson, Ibid, 21 (1888), 415
Meldola & East, JACS, 3 (1888), 460
Meldola & Morgan, Ibid, 3 (1888), 653
Goldschmidt & von Ehow, Ber. 23 (1890), 496
Goldschmidt & Brülcker, Ibid, 24 (1891), 2306
McPherson, Ibid, 25 (1892), 2413
Hantsch, Ibid, 32 (1899), 2100
Mühlau & Strothoff, Ibid, 33 (1900), 855
Mühlau & Krop, Ibid, 33 (1900), 2973
Henges, Ind. Chim. Acta, 8 (1925), 720
Hodgson & Rosenberg, JACS, 56 (1934), 2787
Beadley & Robinsson, Ibid, 56 (1934), 135; cf. JSDC, 51 (1935), 37
Rowe & Dangerfield, JSDC, 52 (1936), 45

40:50

12085  C.I. Pigment Red 4 (Yellowish red, tint Reddish orange)

\[
\text{ClOO}N\text{HO}
\]

2-Chloro-nitrosamine \(\rightarrow\) 2-Naphthol

Discoverers — W. Herzberg and O. Spengler 1907
Agfa, USP 665587; PP 368259; GP 190301 (Fr. II, 704)
\(\text{BIOS 1661}, 137\)
\(\text{FIAT 764} \rightarrow \text{Permanentrot R}\)
Whitmore & Rovaskas, JACS, 62 (1940), 1687

Standard — BS 3591/3 C.I. Pigment Red 4 (Chlorinated p-nitrosamine Red)

Slightly soluble in ethanol, acetone and benzene
HCl conc. — bluish magenta; on dilution — yellowish red ppt.
HNO\(_3\) conc. — bright vermillion
NaOH dil. — no change
Alcoholic KOH — violet solution
12120 C.I. Pigment Red 3 (Yellowish red)

Badische Co., BP 19100/05; FP 357853; GP ap. F20255 (Fr. 8, 723)
BIOS 1651, 49; BIOS 961, 114
FIAT 764 — Hansarot B
Shiraiishi, J. Chem. Ind. Tok. 22 (1919), 99
Rowe & Levin, JSAC, 37 (1921), 303
Everest & Wallwork, Ibid. 44 (1925), 102
Whitmore & Revukas, JACS, 62 (1940), 1657

Standards
BS 3599/1 C.I. Pigment Red 3 (Toluidine Red)
Holland NEN 1964 5271 Pigments. Test methods for Toluidine Red
M.p. 258°C
Slightly soluble in ethanol, acetone and benzene
H₂SO₄ conc. — deep reddish violet; on dilution — orange ppt.
HNO₂ conc. — dull vermilion
NaOH dil. — no change

2-Nitro-β-toluidine → 2-Naphthol

12140 C.I. Solvent Orange 7 (Reddish orange)

M.L.B., BP 5767/82; USP 305546; GP 29087 (Fr. 1, 549)
Bisulfite compound
FIAT 764 — Sudanorange R
Mühlhäuser, Dyes. 264 (1987), 218
Rowe & Levin, JSAC, 40 (1924), 227
Cross, Ibid. 61 (1945), 75

M.p. (from glacial acetic acid) 165°C
Soluble in ethanol, acetone and benzene (reddish orange)
H₂SO₄ conc. — crimson; on dilution — crimson, then orange to reddish brown ppt.
HNO₂ conc. — bright orange solution, becomes duller
NaOH 10% — insoluble (bleeds yellowish)
Alcoholic solution + HCl conc. — orange solution;
+ NaOH conc. — redder

2,4-Xyldiene → 2-Naphthol

12150 C.I. Solvent Red 1 (Yellowish red → Reddish orange)

Discoverer — P. Griess 1899
Badische Co., USP 213355; GP 12451 (Fr. 1, 361)
FIAT 764 — Sudanrot G
Viles, JSAC, 30 (1914), 106
Rowe & Levin, Ibid. 40 (1924), 227

M.p. (from glacial acetic acid) 180°C
Soluble in ethanol (red; on boiling)
H₂SO₄ conc. — claret red; on dilution — dark red ppt.
Alcoholic solution + HCl — wine red;
+ NaOH — orange

12315 C.I. Pigment Red 22 (Red)

Discoverers — A. Winther, A. Laska and A. Zitscher 1911
Patents as for C.I.12300

5-Nitro-β-toluidine → 3-Hydroxy-2-naphthanilide

12355 C.I. Pigment Red 23 (Bluish red)

Discoverers — A. Winther, A. Laska and A. Zitscher 1911
Patents as for C.I.12335

5-Nitro-α-anisidine → 3-Hydroxy-3'-nitro-2-naphthanilide
12485  C.I. Pigment Red 146 (Red)

3-Amino-p-anisidine → 4'-Chloro-3-hydroxy-2',5'-dimethoxy-2-naphthylamide

12516  C.I. Pigment Red 183 (Ulluish red)

2-Methoxy-N,N'-dimethylsulfanilamide → 3-Hydroxy-N-(2-oxo-5-benimidazolyl)-2-naphthylamide

12770  C.I. Disperse Yellow 4 (bright greenish yellow)

Aniline → 2,4-Quinolinediol

Disperser — E. Fussenegger 1905
Badische Co., BP 11205/05; USP 606077; GP 165327 (Fr. 8, 718)
Brü. Dye Corp., BP 236037
Roe, IIIC Lectures, 36
Green, Thorsæ, 1, 41
For preparation of coupling component see —
BP 117167 (Fr. 6, 1221)
Soluble in ethanol, acetone and toluene

20040  C.I. Pigment Yellow 16 (Greenish yellow)

2,4-Dichlorotoluidide (2 mol) → 4:4'-Bi-o-acetocetotoluidide

21095  C.I. Pigment Yellow 14 (Yellow)

2,4-Dichloroacetanilide → 2,4'-Acetocetotoluidide (2 mol.)

21100  C.I. Pigment Yellow 13 (Yellow)

3,4-Dichloroacetanilide → 2,4'-Acetocetotoluidide (2 mol.)

21110  C.I. Pigment Orange 13 (Reddish orange)

3,4-Dichlorobenzonitrile → 3-Methyl-1-phenyl-5-pyrazolone (2 mol.)

Discoverer — A. Laska 1910
Griesheim-Elektro, BP 1730/11; USP 1001286; EP 425429;
GP 236356 (Fr. 19, 937)
BIOS 1661, 122
FlAT 764 — Permanentorange G
H₂SO₄ conc. — bluish scarlet; on dilution — reddish orange ppt.
HNO₃ conc. — brownish scarlet
<table>
<thead>
<tr>
<th>Code</th>
<th>Name</th>
<th>Formula</th>
<th>Properties</th>
</tr>
</thead>
</table>
| 26050 | CI. Solvent Red 19 (Bright bluish red) | C₆H₄HN | Soluble in ethanol (carmine)  
Very soluble in acetone and benzene  
H₂SO₄ conc. — brilliant greenish blue; on dilution — bluish violet to brownish |
| 26100 | CI. Solvent Red 23 (Yellowish red) | N₂N → N₂N | p-Phenylazoaniline → N₂N-2-naphthylamine |
| 26105 | CI. Solvent Red 24 (Red) | N₂N | 4-o-Tolylazo-o-toluidine → 2-Naphthol |
| 26125 | CI. Solvent Red 27 (Bluish red) | N₂N | Xylylazoxydine → 2-Naphthol |
| 26150 | CI. Solvent Black 3 (Black) | N₂N | Aniline → 1-Naphthylamine → 2,3-Dihydro-2,2-dimethylperimidine |
| 51050 | CI. Mordant Blue 35 (Greenish→ Reddish navy) | N₂N | Redisch Co., GP 270879 (Fr. 11, 3197)  
FIAT 764 — Sudanschwarz BN, BT, 413 |
| 51120 | CI. Mordant Blue 56 (Greenish blue) | N₂N | Soluble in water (pale bluish green)  
H₂SO₄ conc. — pale reddish brown (violet on addition of MnO₂);  
on dilution — brownish  
Aqueous solution + NaOH — oxidation to violet |

**Note:** The yield is improved by blowing air into the mixture while heating to prevent the formation of leuco-Gallocyanine, which does not condense with aniline.
51300 C.I. Direct Blue 106 (Height blue)

Condense 5-amino-2-aminophenylsulfonic acid with chlorine in water in presence of magnesium oxide as acid binding agent, cyclise the product in the presence of oleum and isolate as divalent salt.

51310 C.I. Direct Blue 109 (Greenish blue)

Condense 1-phenylamine with chlorine, cyclise to dianiline in boiling nitrobenzene, tetrasulfone with oleum, and convert to tetrasodium salt.

51319 C.I. Pigment Violet 23 (Light violet)

Condense 3-amino-9-ethylcarbazole with chlorine in trichlorobenzene.

56055 C.I. Acid Black 47 (Light grey)

Sulfonated

Condense 3-amino-3-hydroxy-1,4-naphthalic anhydride with aniline and sulfuric acid.

Discoverers: Brunner, Greune, Thiele, and Thiers 1928
I.C., RE 149183; USP 2114405
BPI 1482, 11, FIAT 1313, 3, 252
FIAT 764 — Siriusblau FG Blau.
Slightly soluble in benzene, carbon tetrachloride
Insoluble in alcohol (cold), standard solvent

H₂SO₄ conc. — yellowish red; on dilution — reddish yellow ppt.
NaOH — violet

**Discovery** — Robiquet and Colbin (from Madder) 1926
C. Graefe and C. Liebermann (1871)
C. Graefe, C. Liebermann, and H. Caro (1871)
W. H. Prout (1870)

Graefe & Liebermann, BP 3580/68; USP 95465
Graefe, Liebermann & Caro, HP 1916/60; USP 15/36
W. H. Prout, HP 1948/69, 1918/6
Dale & Schumann, HP 2107/60
M. L. II, HP 2649/72, 5414/91; GP 17627 (Fr. 1, 309), 81230 (Fr. 4, 334)

Auerbach & Gerson, HP 1260/74
Bayer, Wessely & Sickle, HP 2071/74
Hoernerling & McGowan, HP 1712/75
Simpson, Brooke & Ravel, HP 851776
Donner & Marxell, HP 2784/80
König, BP 2136/81
Brönnert, BP 7298/82

**Other Uses**

Heller, GP 36259 (Fr. 1, 309)
Teverkut & Söchnir, GP 38454 (Fr. 1, 309)

Scheeff, HP 2001/61; 2159/64

Badische Co., BP 7735/04, 20664/11; PP 344680; GP 165536

(Fr. 5, 237); 285720 (Fr. 12, 431)

Bayer Co., BP 1964/108; 28541/11; 34624/11; 1105/12;
USP 1036080; 1036831; PP 25137; 451118; A. P. 23191;
GP 241606; 259597 (Fr. 10, 594, 595), 249658, 251253 (Fr. 11, 386, 387)

Griesheim-Elektron, BP 16659/1; USP 1150515; PP 475411; GP 292247 (Fr. 12, 432)

Scottish Dyes, BP 174101, 246579, 291328; USP 1744813
BIO 1848, 39; PLAT 765 — Alizarinrot B, GP 27

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32, 320, 305; 3 (1870), 359, 636; Ann. Soc. Fil. 7 (1870), 391
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319; J. Soc. Arts, 27 (1879), 349; JCS, 23 (1873), 133;
1873, 595; 37 (1850), 554; 69 (1850), 627

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Claus, Ber. 8 (1875), 330
Widman, Ber. 9 (1876), 856
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Schunck & Römer, Ber. 10 (1877), 175; 13 (1880), 42
Liebermann & Boeck, Ber. 11 (1878), 1613
von Feger, J. prakt. Chem. 18 (1875), 293

Goppenreiter, Dingl. 224 (1878), 96; JSC, 2 (1882), 63
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Lavitsstein, JSCI 2 (1883), 213
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JSCI, 22 (1903), 605
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Leigt, JSCD, 32 (1916), 205

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**Note** — For information on naturally occurring Alizarin see C.I.75530

**Chromium-Dull bluish red; Iron-Dull purple**
**SS050**

**Smoke Dye (Orange)**

**SS050: 1** C.I. Permanent Violet 12 (Aluminium salt-Violet)

**Classical name:** Quinizarin

(a) Treat anthraquinone with sulfuric acid in the presence of boric acid, boric acid and mercury, boric acid and nitrous acid or nitrosonium acid and mercury.

(b) Treat 1-hydroxyanthraquinone or 2-hydroxyanthraquinone with sulfuric acid in the presence of boric and nitrous acids.

(c) Treat 1-hydroxy-4-nitroanthraquinone or 1,4-dihydroanthraquinone with sulfuric acid in the presence of boric acid.

(d) Condense phthalic anhydride and phenyl hydroxylamino in the presence of Liebermann & Jellinek.

- Zahn, Reynolds & Bigelow, JACS, 45 (1926), 420
- Lagodanski, M. Hahn, Fierm-David, Zahn & Reynolds, JACS, 45 (1926), 420
- Lagodanski, M. Hahn, Fierm-David, Zahn & Reynolds, JACS, 45 (1926), 420
- Liebermann, Ann. 183 (1876), 134; 212 (1882), 11; 187 (1877), 607; 11 (1878), 160; 35 (1902), 1496
- Peter, Z. Anal. Chem., 76 (2) (1907), 139
- Wolf, Ber. 39 (1906), 205

- Silver in ether
- H$_2$SO$_4$ conc. — greenish yellow fluorescence

**SS8500**

**C.I. Mercurial Violet 26 (Chromium-Violet)**

**Classical name:** Quinizarin

[a][b][c][d]

**Oxidize alizarin or quinizarin with a large excess of fuming sulfuric acid and hydrolyse**

- M. Hahn, Fierm-David, Zahn & Reynolds, JACS, 45 (1926), 420
- Lagodanski, M. Hahn, Fierm-David, Zahn & Reynolds, JACS, 45 (1926), 420
- Liebermann, Ann. 183 (1876), 134; 212 (1882), 11; 187 (1877), 607; 11 (1878), 160; 35 (1902), 1496
- Peter, Z. Anal. Chem., 76 (2) (1907), 139

- Silver in alcohol
- H$_2$SO$_4$ conc. — bluish violet; on dilution — dull red ppt.

**60710**

**C.I. Disperse Red 15 (Bluish pink — Bluish red)**

(a) Partially aminate leuco-quinizarin with aqueous ammonia under pressure.

(b) Nitrates 1-hydroxyanthraquinone in sulfuric acid in the presence of boric acid. Reduce the 1-hydroxy-4-nitroanthraquinone formed with aqueous sodium sulfide.

(c) Nitrates 1-methoxyanthraquinone, hydrolyse and reduce.

(d) Hydrolyse 1-benzeno-4-chloroanthraquinone.

- Breslow, 227, 239, 260, 266
- Fierz-David, 542
- Houben, 320, 330, 366, 370

**Discoverer — E. Schmidt 1909**

- Bayer, BP 8723/90, 1712/91, 4871/91; USP 446923; GB 60855; 60693, 67063; (Fr. 3, 198, 203, 203)
- BRS 1485, 27
- Liebermann & Wiese, Ber. 20 (1887), 863
- Grabe, Ber. 23 (1890), 3739; Ann. 249 (1905), 205
- Schmidt, J. prak. Chem., 43 (1891), 1; 217; Bull. Soc. Ind. Miullhuse, 64 (1913), 239
- Hahn, Wolf & Jüger, Ber 57 (1924), 1394
- Breslow, Z. anal. Chem. 76 (1929), 354
- Breslow, 227, 239, 260, 266
- Fierz-David, 542
- Houben, 320, 330, 366, 370

- Soluble in alcohol
- H$_2$SO$_4$ conc. — bluish violet; on dilution — dull red ppt.
61105 C.I. Disperse Violet 4 (Bright bluish violet)

C.I. Solvent Violet 12 (Bright bluish violet)

(a) Methylate leuco-1,4-diaminoanthraquinone with methanol in sulfuric acid in the presence of chlorine

(b) Treat leuco-quinizarin with ammonia and methylene and oxidise

Soluble in acetone, benzene
Slightly soluble in alcohol
Insoluble in linseed oil
H_2SO_4 conc. --- brown; on dilution --- red

61110 C.I. Disperse Blue 19 (Bright reddish blue)

C.I. Solvent Blue 68 (Reddish blue)

Condense 1-amino-4-hydroxanthraquinone with aniline in the presence of boric acid

Soluble in acetone, alcohol, benzene, Cellosolve
Slightly soluble in carbon tetrachloride
H_2SO_4 conc. --- dull bluish violet; on dilution --- dull blue ppt.

61500 C.I. Disperse Blue 14 (Bright blue)

Treat quinizarin under pressure with aqueous methyamine and sodium hydrosulfite or zinc dust. Oxidise the leuco compound with nitrobenzeno, or hot sulfuric acid

Soluble in acetone, alcohol, glacial acetic acid, nitrobenzene, pyridine, toluene
H_2SO_4 conc. --- reddish brown

61505 C.I. Disperse Blue 3 (Bright blue)

(a) Condense methylamine and ethyamine with quinizarin and leuco-quinizarin in isobutanol and oxidise

(b) Condense 1-bromo-4-methylaminoanthraquinone with ethanolamine in presence of copper acetate

Soluble in acetone, alcohol, benzene, Cellosolve
Slightly soluble in carbon tetrachloride
Insoluble in Stoddard solvent
H_2SO_4 conc. --- brown; on dilution --- dull red

*61515 C.I. Disperse Blue 24 (Bright blue)

Brominate 1-methylaminoanthraquinone and condense with aniline

Soluble in acetone, alcohol, benzene

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Note: According to BIOLS 987, 1,4-bis(methy lamino)- and 1,4-bis(2-hydroxyethylamino)anthraquinones are also present.
REFERENCES


