

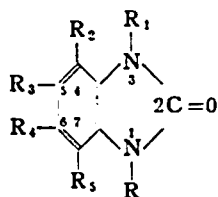
## 2(3H)-Benzimidazolones as Stabilizers for Smokeless Powders

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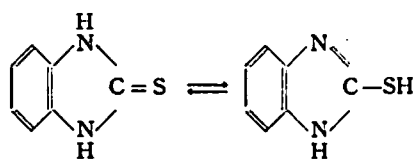
The centralites, mainly 1, 3-dialkyl-1, 3-diphenylureas, were initially used in the manufacture of smokeless powders as gelatinizers for nitrocellulose and as deterrents for progressive burning powders (in accordance with the conventions of the Chemical Abstracts, the term "Centralite I" is used to refer to 1, 3-diethyl-1, 3-diphenylurea). In 1926 Apard<sup>1)</sup> suggested that the benzene nuclei in the molecule should permit it to react with the decomposition products of a powder, and hence to act as a stabilizer. Thus, well-defined dinitro- and tetranitro-derivatives of centralite have been shown to be obtained from nitration of centralite with nitric acid alone or in mixture with sulphuric acid. Similar results were also obtained by Masaki<sup>2)</sup>.

Lecorché and Jovinet<sup>3)4)5)</sup>, in a trial to explain the stabilizing action of centralite, assumed that centralite is only an inert constituent of the powder until decomposition of the major constituents occur: the nitrocellulose and the nitroglycerine produce traces of acids, whereby hydrolysis of centralite leads to the formation of N-ethylaniline. The latter reacts with nitrous acid to form N-nitroso-N-ethylaniline, while nitric acid yields, at least in part, mononitrocentralite.

The present investigation deals with the possibility of finding organic compounds which may show superior properties as stabilizers than centralite, and correlation between such properties with the structure of the compounds under investigation.

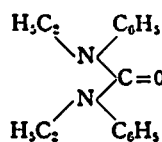


- Ia, R=R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H.
- b, R=CH<sub>3</sub>; R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H.
- c, R=R<sub>1</sub>=CH<sub>3</sub>; R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H.
- d, R=C<sub>6</sub>H<sub>5</sub>; R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=H.
- e, R=R<sub>1</sub>=R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H; R<sub>3</sub>=CH<sub>3</sub>.
- f, R=R<sub>1</sub>=R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H; R<sub>3</sub>=NO<sub>2</sub>.
- g, R=R<sub>1</sub>=R<sub>2</sub>=R<sub>5</sub>=H; R<sub>3</sub>=R<sub>4</sub>=NO<sub>2</sub>.
- h, R=R<sub>1</sub>=R<sub>5</sub>=H; R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=NO<sub>2</sub>.
- i, R=R<sub>1</sub>=H; R<sub>2</sub>=R<sub>3</sub>=R<sub>4</sub>=R<sub>5</sub>=NO<sub>2</sub>.



IIa

IIb



III

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2(3H)-Benzimidazolones(o-phenyleneureas) bear structural resemblance to the centralites e. g. 1,3-dialkyl-1,3-diphenylurea; they may be considered as cyclic urea derivatives. The parent compound (Ia) exhibits a high degree of chemical stability. This is evidenced by its resistance to the action of concentrated hydrochloric acid at 200°C, and its stability to distillation over red hot zinc dust. Parallel to centralite (1,3-diethyl-1,3-diphenylurea) (III), it is sparingly soluble in cold water. 2(3H)-Benzimidazolone (Ia) is a very weak base, it dissolves in concentrated hydrochloric acid, but is precipitated unchanged by dilution with water<sup>9)</sup>.

Thus, in the following are results obtained by use of 2(3H)-benzimidazolone (Ia) and its derivatives (Ib-f) for centralite under the standard test conditions.

#### Experimental Results

Samples of double-base smokeless powders were manufactured by a solventless process using 3% 2(3H)-benzimidazolone (Ia) or its derivatives (Ib-f) as stabilizers. Dinitrotoluene (8%) and dibutylphthalate (4%) were added in each case, except in the case of the ballistite powder, where only Ia was added to the calculated amounts of nitrocellulose and nitroglycerine. A standard sample was stabilized with centralite (III); meanwhile, a nonstabilized sample was prepared and used as "reference sample".

The samples were shaped in the form of flakes and then subjected to the various stability test:

#### (A) Qualitative stability tests.

##### i) International test at 100°C<sup>7)</sup>.

From the results recorded in table I, it is obvious that the stabilizing effect of Ia (9-10 days) is nearly the same as that of III (10-11 days). Monosubstitution of the imino hydrogen in position-1 with a methyl or phenyl group led to a

slight drop in the stabilizing effect (9-10 days). On the other hand, substitution in the 5 (or 6)-position by a methyl group reduced the stabilizing properties (7-8 days). In case of Ic, marked loss in the stabilizing effect was observed (4-5 days). The introduction of a nitro group in the 5 (or 6)-position, e. g. If, rendered the smokeless powder unstable and effected rapid decomposition (less than one day which was rather less than the stability of the reference sample (1-2 days)). In the case of the powder stabilized with 2-mercapto-2(3H)-benzimidazole (II), the stability was too low; rapid deterioration was observed after 3 hours.

##### ii) The German test at 120° (Brown fumes)<sup>8)9)</sup>.

From the results recorded in Table I, it is found that Ia and III have same stabilizing effect and the order of this effect is Ib (12 hours), Ie (11 hours), Id (10 hours) and Ic (7 hours). The markedly low stabilizing properties shown by If (1½ hours), being less than the reference sample, may illustrate the induced effect of the nitro group. In the case of the powder stabilized by II, explosion occurred after 20 minutes.

##### iii) The Methyl-violet test<sup>10)</sup>. This test is essentially used for the measure of stability of nitrocellulose, but it is also used with some modifications for testing double-base propellants<sup>11)</sup>.

From the results recorded in Table I, it is obvious that the decolorization of the standard test paper started at the same time in the case of both Ia and III (35 minutes), while the time elapsing till it exhibited the salmon-pink colour was longer in the case of Ia (115 minutes) than in the case of III (90 minutes). No brown fumes appeared after continuation of heating for further 5 hours. Substituted derivatives showed less stabilizing

Table I Results of the stability tests

Stabilizer used in the powder	International Test at 100°C (in days)	German Test at 120°C (hours)	Methyl violet test at 120°C (minutes)	Hansen-Metz Test at 110°C (pH value after 8 hours)	Bergman-Junk Test at 120°C (ml. of NO /5 g.)	The Dutch Test at 105°C (loss in weight after 64 hours)	Ignition Temperature 5°C/minute
Reference sample	1- 2	2	Start of change: 20 Salmon pink : 60 Brown fumes : 90	2.8	10.0	Brown fumes	161.9
III	10-11	17	Start of change: 35 Salmon pink : 90 Brown fumes : —	3.6	3.8	0.79 <sup>1</sup> / <sub>2</sub>	173.0
Ia	9-10	17	Start of change: 35 Salmon pink : 115 Brown fumes : —	3.8	2.0	0.24%	174.6
Ib	9-10	12	Start of change: 20 Salmon pink : 50 Brown fumes : —	3.55	2.4	0.37%	176.5
Ic	4- 5	7	Start of change: 30 Salmon pink : 70 Brown fumes : —	3.3	4.5	0.76%	169.0
Id	7- 8	10	Start of change: 25 Salmon pink : 60 Brown fumes : —	3.6	2.2	0.40%	172.0
Ie	6- 7	11	Start of change: 30 Salmon pink : 60 Brown fumes : —	3.4	2.5	0.61%	178.2
If	<sup>1</sup> / <sub>(15 hours)</sub>	1 <sup>1</sup> / <sub>2</sub>	Start of change: 20 Salmon pink : 45 Brown fumes : 75	2.8	8.1	Brown fumes	
II	<sup>1</sup> / <sub>(3 hours)</sub>	Explosion	Start of change: 5 Salmon pink : 10 Brown fumes : 15	Brown fumes	Brown fumes	Brown fumes	
Balistic sample using Ia			Start of change: Salmon pink : Brown fumes :	3.4	2.8		

power as illustrated in Table I and the order is as follows;  $I_b > I_d > I_c > I_e$ . The 5 (or 6)-nitro derivative (If) showed also a marked unstabilizing effect to the extent that brown fumes appeared after 75 minutes of continuous heating, whereby, in the case of the reference sample brown fumes appeared after 30 minutes. The thio-derivative (II) rendered the powder so unstable that brown fumes appeared after 15 minutes.

(B) Quantitative Stability Tests:

i) Hansen-Metz Test at 110°C (Hydrogen ion concentration method)<sup>123</sup>.

From the results recorded in Table I, it is apparent that the powder stabilized with Ia showed the best stability (pH value of 3.8 after 8 hours). The powder stabilized with Id showed stability similar to that of the powder stabilized with III (pH value of 3.6 after 8 hours). Ib imparted nearly the same stability (pH value of 3.55

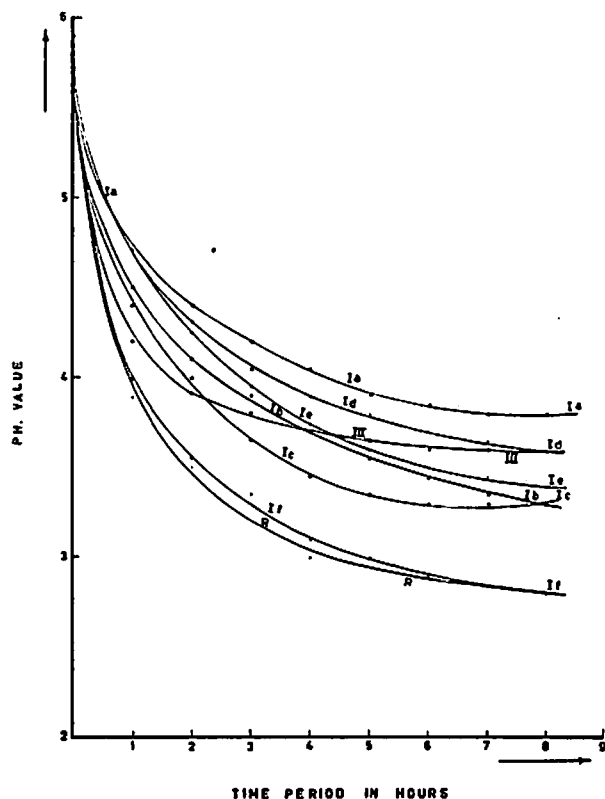


Figure 1 Hansen-Metz Test

after 8 hours). The powders containing Ic and Ie showed a lowered stability (pH values of 3.3 and 3.4 after 8 hours respectively). The powder, containing If as well as the reference powder, showed a marked low stability (pH of 2.8 after 8 hours), while the powder containing II was so much unstable that brown fumes were quickly formed and the test was not completed (cf. Fig. 1).

ii) Bergmann-Junk Test at 120°C<sup>133</sup>:

The results tabulated in Table I indicated that Ia acted as the best stabilizer since only 2.0 ml. nitric oxide were formed from 5 g. of the sample. Id, Ib, and Ie showed better stabilizing effect (2.2 ml., 2.4 ml., and 2.5 ml. of nitric oxide respectively) than III (3.8 ml. of NO), while Ic showed less stabilizing effect (4.5 ml. of NO). The 5-nitro derivative (If) showed a very low stabilizing effect (8.1 ml. of NO) as compared with that of the reference powder (10.0 ml. of NO). II caused the evolution of brown fumes before completion of the test.

iii) Determination of the loss in weight at 105°C (The Dutch test<sup>144</sup>):

The data recorded in Table I, showed a very distinct stabilizing effect for Ia (0.24%). The percentage of loss in weight after 64 hours recorded for the powders containing Ib, Id, and Ic (0.37%; 0.40%; and 0.61% respectively) were less than that of the powder containing III (0.79%). In the case of the powders stabilized with If and II, as well as the reference sample, brown fumes were evolved before completion of the test, and hence caused the test to be stopped. The loss in weight was graphically represented as a function of the time of heating (cf. Fig. 2)

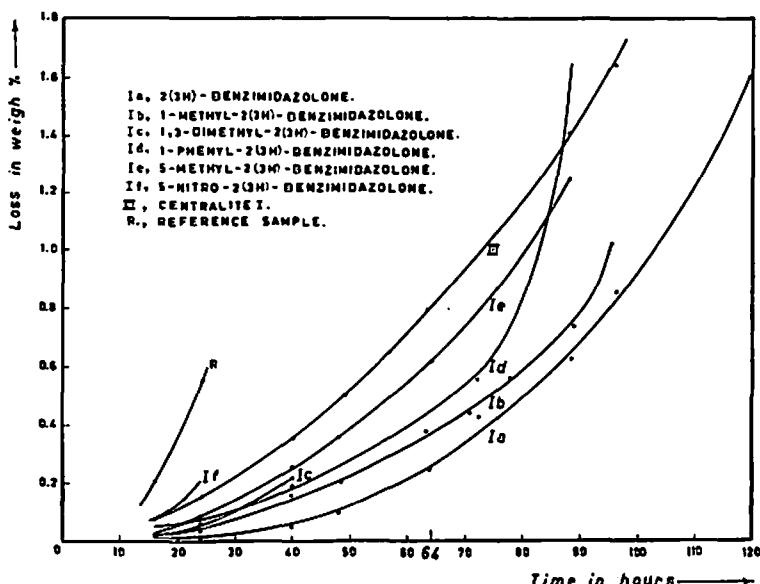


Figure 2 Dutch Test

### Chromatographic Study

In the present investigation a one-dimensional method (TLC) was used to separate nitro derivatives (If-Ii) which may be possibly formed during the accelerated aging of a ballistic smokeless powder stabilized with 3% of Ia.

Authentic samples of the nitro derivatives, If, Ig, Ih and Ii were prepared according to the method described by Effros and his co-workers<sup>15,16</sup>. A 10 g. sample of the ballistite was subjected to the 100°C test until the appearance of clearly visible brown fumes (from 6-7 days). After cooling, the sample was extracted in a Soxhlet assembly using about 125 ml. of dry ether-chloroform mixture (1 : 1) for 24 hours. The mixture of solvents was then evaporated under reduced pressure and the residue was dissolved in about 10 mls. of absolute alcohol.

Transfer of the sample to the silica gel G plate was carried out by means of a melting point capillary tube. The width of the applied band was kept at approximately 15mm.

Transfer of the authentic samples (nitro derivatives of Ia) was done in the same way. The distance between the bands was not less than 5mm. The arrangement of the bands was as follows: If-sample-Ig-sample-Ih-sample-Ii-sample.

After applying the solvent (ethylalcohol/benzene in the ratio of 7:93), six compounds were completely separated from the sample.  $R_F$  values of If, Ig, and Ih were found to be in agreement with those of three compounds separated from the sample. All compounds separated were self-indicator and could be easily detected without any further treatment. However, the separated compounds were more clearly distinguished by spraying the plate uniformly with concentrated ammonia solution to intensify their natural colours. Using  $R_F$  measurements, natural colours, and colours developed after spraying, it was possible to confirm the presence of If, Ig, and Ih.

$R_F$  values of three other unknown compounds separated from the sample are also given in table II:

Table II  $R_F$  values of derivatives of Ia after accelerated aging.

Compound	$R_F \times 100$
If	23
Ig	22
Ih	18
Ii	0
Unknown 1	94
" 2	48
" 3	32

### Discussion of the Results

It is clear from the results given in table I that 2(3H)-benzimidazolone (Ia) possesses marked superior stabilizing effect than the commonly used centralite (III). This may be clearly shown from the accepted standard test, e. g. "the Dutch test" (cf. Fig. 2).

Remarkable is that substitution of the imino hydrogens in Ia is accompanied with lowering the stabilizing properties.

Complete substitution, as in the case of 1,3-dimethyl derivative (Ic), leads to lower stability than the mono N-substituted products, i. e. Ib and Id.

Study of the effect of substitution of the benzene ring in Ia reveals the importance of the 5 (or 6)-position. Thus, substitution in this position with a methyl group (cf. Id) was found to show some stability properties but less than those shown by the N-substituted products. On the other hand, substitution by a nitro group in the same position (cf. If) seems not to fulfill the necessary requirements as a stabilizer which may be related to the induced effect of the nitro group in position-5 (or 6). This finds analogy with the observation that introduction of nitro group or groups in the benzene nuclei of a stabilizer, e. g. diphenylamine is accompanied with increase of the acidic properties, and thus lowering the stabilizing properties<sup>17)</sup>.

Finally, using 2 (3H)-thiobenzimidazolone

(IIa) which is known to be preferentially present as 2-mercaptobenzimidazole (IIb) (cf. the formation of S-alkylation products upon treatment with alkylating agents<sup>18)19)20)</sup> as well as its ready oxidation with iodine to form the corresponding disulphide<sup>21)</sup> has led to very poor results, which may be related to its ready oxidation.

Further insight in the mechanism of the stabilizing action of Ia and its substituted products (Ib-f) can find support from the behaviour of the structurally related stabilizers, namely III and diphenylamine. Shroeder and his co-workers<sup>22)</sup> succeeded by the use of the chromatographic spectrophotometric methods to identify many of the derivatives that are formed from III during the accelerated aging of double-base smokeless powders. Moreover, quantitative determinations showed that the percentage of III influenced the composition of the decomposition products. Chromatographic methods were also used by Shroeder et al.<sup>23)</sup> for the separation of the derivatives of diphenylamine, mainly nitro and nitro-nitroso-derivatives.

Recently, Yasuda and his co-workers<sup>24)</sup> have succeeded by the application of thin layer chromatography technique to effect the separation and identification of some of the formed nitro derivatives from diphenylamine used as a stabilizer in smokeless powders.

A general study of the chemical nature of the stabilizers, i. e., centralite and diphenylamine favours the classical mechanism of nitrosation, rearrangement and oxidation (cf. Schroeder, and his co-workers<sup>23)</sup>). With certain degree of assurance, the following steps may be taken into consideration: (a) N-nitrosation, (b) denitrosation and (c) direct nitration. An observation which may also be taken in favour of the suggestion<sup>17)25)</sup> by Aparé is that the benzene nuclei in the

molecule of a stabilizer should react with the decomposition products of the powder. In analogy, one may carefully accept this views which may find support that nitrogen dioxide produced as the formed nitric acid during the nitrocellulose as well as nitro-glycerine, react with Ia to give a mixture of nitro derivatives.

That Ia and/or Ic have been reported to be directly nitrated with nitric-sulphuric acids mixtur<sup>15)16)</sup> at different temperatures to yield 5 (or 6)-nitro-(If), 5, 6-dinitro-(Ig), 4, 5, 6-trinitro-(Ih) and 4, 5, 6, 7-tetranitro-(Ii) derivatives, may support the view that the benzene nucleus in Ia reacts with the decomposition products of the powder. This is indeed the case obtained from the thin-layer chromatographic experiment on an accelerated aged double-base smokeless powder using I as a stabilizer. Successful separation and identification of the mononitro-(If), dinitro-(Ig) and trinitro-(Ih) as well as the detection of other three products developing positive colour with alkaline reagents (possibly other nitro compounds) gave an insight in the mechanism of the stabilizing action of Ia and its substituted derivatives (Ib-Ie). Furthermore, the formation of these nitro derivatives during the aging process after prolonged heating in contact with the decomposition products may find support from the ready transformation of the mononitro to the di-, tri- and tetranitro derivatives<sup>15)16)</sup>.

That the benzimidazolthione (IIa) gave poor results may be related to the fact that it is readily oxidized to the disulphide by the action of nitric acid, formed during the decomposition of the components of the double-base smokeless powder. The disulphide will lead to further decomposition products under the given experimental conditions.

Further work is in progress to study the nature of the decomposition products of Ia

and its substituted derivatives (Ib-f) to enlighten the mechanism of the stabilizing action of such type of compounds.

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## 無煙火薬用安定剤としての 2(3H)-Benzimidazolone

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2(3H)-Benzimidazolone およびその誘導体, すなわち 1-methyl, 1,3-dimethyl-, 1-phenyl, 5-methyl-, 5 (又は 6)-nitro-2(3H)-Benzimidazolone および 2(3H)-thiobenzimidazolone を製造し安定剤としてダブルベース無煙火薬に混合した。

これらの安定剤を含んだ火薬について種々の安定度

試験を行い, セントラリット I (1,3-diethyl-1, 3-diphenylurea) を含む場合および安定剤を含まない場合を比較した。

無煙火薬の分解生成物中から薄膜クロマトグラフを用いて nitro-2(3H)-benzimidazolone を分離同定した。