

Reduction in Acidity of RDX and its Compositions by Use of Suitable Additives

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Received 13 April 1981; revised 16 January 1982

Abstract. Calcium Silicate and Zinc Stearate have been used as additives to reduce the acidity of RDX and RDX/TNT compositions. They have been found to be effective in reducing the acidity of RDX/TNT compositions but ineffective for RDX alone. An explanation to this effect has been provided.

1. Introduction

RDX (i.e. Cyclotrimethylene trinitramine, also known as cyclonite) is manufactured by two well known processes e.g. Nitrolysis and acetic-anhydride process. The former process is followed in many countries including India. In this process, there is a lot of material wastage due to higher acidity content of RDX (generally when total acidity calculated as HNO_3 is above 0.05%) which is not considered suitable for use in ammunitions as higher acidity increases risk in handling/transportation and further processing of the compositions and also reduces the shelf life of the ammunitions.

On literature survey it was found that attempts have been made from time to time to reduce the acidity but in no case appreciable reduction was obtained. Though there are some references indicating the use of additives as antacid in RDX compositions but details were not found in the literature. This created interest to look deeply into the problem of RDX acidity and to find out a suitable and easier method which could be adapted safely for large scale production.

This paper reports the study in detail, on laboratory scale, on the effect of some suitable additives viz. Calcium Silicate and Zinc Stearate in reducing the acidity of RDX and its compositions.

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Attempt has also been made to explain the mechanism of action of the additives in reducing the acidity of the compositions.

2. Experimental

Acidity of RDX has been determined by dissolving the material in acetone, adding an equal volume of distilled water and titrating with standard alkali using a mixed methyl red bromocresol green indicator. In case of RDX/TNT, the composition is dissolved in acetone, equal volume of carbon tetrachloride is added and then water (about five times of the volume of acetone used) is added with vigorous stirring and the resultant solution is titrated with standard alkali using methyl red as indicator.

For the preparation/manufacture of RDX/TNT (80 : 20), RDX is held in suspension under vigorous stirring in hot water, to which required quantity of TNT is added. The final product is freed from water and then RDX/TNT (60 : 40) is prepared by 'Dry mixing process'. The residual acidity in this mixture essentially depends on the acidity contributed by the RDX as TNT does not contribute to any significant acidity. Therefore, the estimated residual acidity is expressed on the RDX content of the composition.

The additives viz. Calcium Silicate and Zinc Stearate were incorporated separately in various proportions to RDX and RDX/TNT (60 : 40) compositions of various acidity levels. Additives were added in RDX/TNT (60 : 40) during the preparation of RDX/TNT (60 : 40) itself.

In addition to the study of the effect of additives towards the reduction of acidity, their behaviour towards other related parameters has also been studied to find out their acceptability in regular service use. The parameters studied are friction sensitivity, impact sensitivity, sensitivity to electric spark, compatibility, pourability, storage suitability, etc. The trials conducted for the present work are on laboratory scale only (i.e. with batch sizes from 500 gm to 2 kg).

3. Results and Discussion

It is seen from Tables. 1 & 2 that there is an appreciable reduction in acidity on incorporation of the additives in RDX/TNT (60 : 40) but there is practically no reduction of acidity when the additives are directly incorporated to RDX. It is seen that 0.5% Calcium Silicate/1.0% Zinc Stearate reduce considerably the acidity of RDX/TNT (60 : 40) prepared from RDX containing acidity upto 0.09% as HNO_3 .

Incorporation of excess amount of the additives makes the composition alkaline which is also not desirable as alkalinity also may cause adverse effect on the shelf life/storage life of the compositions.

Mechanism of action of these additives with reference to reduction in acidity of RDX compositions, has not been mentioned in the literature available. An attempt has been made to explain it here.

Table 1. Acidity of RDX/TNT (60:40) on incorporation of the additives

| Sl. No. | <i>CaSiO₃</i> | | | Zinc Stearate | | | | | Remarks |
|---------|--------------------------------|--------------------------------------|--|---|---------------------|--------------------------------------|--|---|------------------------------|
| | <i>CaSiO₃</i> added | Acidity (as <i>HNO₃</i>) | Alkalinity (as <i>Na₂CO₃</i>) | Acidity of recovered RDX from the composition | Zinc stearate added | Acidity (as <i>HNO₃</i>) | Alkalinity (as <i>Na₂CO₃</i>) | Acidity of recovered RDX from the composition | |
| | (%) | (%) | (%) | (%) | (%) | (%) | (%) | (%) | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 1. | 0.10 | 0.014 (0.015) | — | 0.046 | 0.2 | 0.013 (0.012) | — | 0.058 | original |
| 2. | 0.15 | 0.003 (Nil as pH 6.2) | — | 0.038 | 0.3 | 0.003 (nil pH 6.25) | — | 0.048 | acidity of RDX/TNT is 0.066% |
| 3. | 0.2 | — | 0.013 | 0.034 | 0.5 | — | 0.003 | 0.047 | |
| 4. | 0.4 | — | 0.053 | 0.012 | 1.0 | — | 0.003 | 0.042 | |
| 5. | 0.5 | — | 0.088 | 0.012 | — | — | — | — | |
| 6. | 1.0 | — | 0.247 | 0.006 | — | — | — | — | |

- Notes :
- (i) Acidity determination has been carried out by normal titration method as well as by potentiometric titration method. Results obtained by both the methods are exactly same with very slight difference at the third place of decimal which is of no significance for the present work.
 - (ii) Acidity figures indicated inside brackets have been obtained by potentiometric method. pH above 6.0 indicates that the solution has become practically acid free.
 - *(iii) % acidity of the recovered RDX from the compositions gives very clear idea of reduction of acidity, RDX is recovered from the composition containing additives as per the method indicated under Table No. 4.

Table 2 . Acidity of RDX/TNT/additives

| Sl. No. | Composition | Acidity* (as HNO_3) |
|---------|---|------------------------|
| 1. | RDX Gr. IA (as such) | 0.041% |
| 2. | RDX Gr. IA/0.25% $CaSiO_3$ | 0.037% |
| 3. | RDX Gr. IA/0.25% Zinc Stearate | 0.038% |
| 4. | RDX/TNT 80 : 20 (prepared by wet process) | 0.035% |
| **5. | RDX/TNT 80 : 20/0.25% $CaSiO_3$ | 0.029% |
| 6. | RDX/TNT 60 : 40 | 0.027% |
| 7. | RDX/TNT 60 : 40/0.5% Zinc Stearate | 0.014% |
| 8. | RDX/TNT 60 : 40/1.0% Zinc Stearate | 0.010% |
| 9. | RDX/TNT 60 : 40/0.5% $CaSiO_3$ | 0.008% |
| 10. | RDX/TNT 60 : 40/1.0% $CaSiO_3$ | 0.004% |

Notes : * (i) Acidity has been determined after recovering RDX from the compositions.

** (ii) Uniform dispersion of $CaSiO_3$ is difficult to get.

(iii) The acidity of the compositions essentially depends only on the acidity of RDX as TNT does not contribute any significant acidity. Therefore, the acidity of the compositions is expressed on the RDX content only.

Acidity in RDX arises out of residual acids retained by the crystals from the mother liquor during manufacture. Part of the residual acids get locked in the interstices of the crystal growth and cannot be washed away by superficial water washes. This is termed as 'occluded Acidity' and is estimated by total dissolution of the crystals in a suitable solvent (e.g. acetone).

Occluded acidity is dependent upon the process control features and is not fully controllable while the surface acidity is fully controllable to almost nil level by effective external washing. At the end of the manufacturing process, the RDX obtained after centrifuging and washing with water, is stabilised by prolonged boiling in water to reduce the surface acidity. RDX, thus, obtained is known as RDX Gr IA.

This RDX Gr IA is further crystallised in acetone to get a material practically free from acidity. This latter type of RDX is known as RDX Gr I but the process involved is an expensive and dangerous due to the flammable nature of acetone used. Therefore, the production of this particular grade is very much limited depending upon very specific requirements.

It is known that RDX partially dissolves in molten TNT during incorporation which may lead to a change in angularity of the crystals. It is, therefore, felt that when RDX is added to molten TNT and stirred during incorporation, the particle size of RDX is decreased to a certain extent and liberates part of the occluded acidity. When, at this stage, an additive is incorporated in the mixture of RDX/TNT, it reacts with the acid liberated and reduces/neutralises the acidity of

Table 3 . Estimation of water soluble Calcium salt on subjecting RDX/TNT (60 : 40)/1% Calcium Silicate to V.S. test (i.e. heating for 40 hours at 120°C)

| | Step of the experiment | Sample subjected to V.S. test | Sample not subjected to V.S. test |
|----|--|-------------------------------|-----------------------------------|
| 1. | Amount of sample taken for analysis | 5.0 g | 4.9871 g |
| 2. | Amount of Calcium Silicate (after acetone wash) | 0.046 g | 0.0498 g |
| 3. | % of Calcium Silicate | 0.92% | 0.9986% |
| 4. | *Water soluble calcium salt (by water wash) | 0.0242 g | 0.0214 g |
| 5. | % water soluble calcium salt found from calcium silicate | 52.60% | 42.97% |

- Notes : (i) 1.5% water solubility of Calcium silicate (V.M. free)
(ii) Solubility of Calcium silicate in 1% HNO_3 is 21%.
(iii) The acidity of RDX used is 0.09%
*(iv) The water wash was found to contain nitrate radical.

the composition. It has been found out experimentally (results shown in Table 3) that additives mostly react at this stage i.e. while mixing additives in molten RDX/TNT mixture, and not so much afterwards. It is seen from the table that calcium silicate added to RDX/TNT (60 : 40) having 0.06% acidity is getting converted to water soluble calcium salt upto the extent of 43%. The water soluble salt was obtained by removing RDX/TNT by washing the composition with acetone and then washing the residue with water. Same experiment was repeated after heating the composition for 40 hours at 120°C. The water soluble calcium salt obtained from the latter sample was of the order of 52%. This indicates that the reaction of the additives with the acid liberated during RDX/TNT mixing in hot condition does not take longer time. In fact by increasing the incorporation time (i.e. mixing of RDX/TNT in hot condition in presence of additive) it does not give better result (i.e. more reduction of acidity).

In order to assess the interference of the additives, if at all, during titration, a few experiments were conducted (result shown in Table 4). In these acidity of RDX/TNT composition was determined by removing the additives from the composition. For this, first TNT was removed from the composition by washing with benzene and then RDX was recovered by acetone washes, leaving behind calcium silicate. The filtrate of acetone wash which contains RDX only was collected. This acetone wash was titrated to get the corresponding value of acidity. Results clearly indicate, that incorporation of 0.5% $CaSiO_3$ to the composition of 0.07% acidity (from original acidity of 0.1%), the acidity reduces to 0.018%. If the acidity would have been determined by normal conventional titration method then the results would have indicated alkalinity as was observed in other experiments (Table 1).

Table 4. Acidity of RDX after recovery from the compositions

| Composition | Experiment 1 | | Experiment 2 | | Remarks |
|---|----------------------|---|----------------------|---|---|
| | RDX/TNT (60 : 40) | RDX/TNT/ CaSiO_3 60/40/0.5% | RDX/TNT (60 : 40) | RDX/TNT/ CaSiO_3 60/40/0.5% | |
| <i>Step 1</i> Amount of composition taken for analysis | 10 g | 10 g | 10 g | 10 g | |
| <i>Step 2</i> Per cent residue of step 1 after extraction with benzene | 60.4 | 60.72 | 60.41 | 59.3 | Original occluded acidity of RDX is 0.10% as HNO_3 . |
| <i>Step 3</i> Per cent residue of calcium-salt left after extraction with acetone | Nil | 0.475 | Nil | 0.48 | |
| <i>Step 4</i> the residue left at <i>Step 2</i> . | | | | | |
| Filtrate from step 3 titrated for % acidity as HNO_3 | 0.074% | 0.018% | 0.073% | 0.016% | |

Note : Under this method composition containing an additive is first washed completely with benzene to remove TNT and then the residue left is washed with acetone to separate RDX. The acetone wash is collected and titrated for getting the acidity of the recovered RDX.

Table 5. Compatibility of the additives with RDX/TNT (60 : 40) compositions (Determined by vacuum stability test at 120°C for 40 hours)

| Sl. No. | Composition | Volume of gas evolved in ml. | Remarks |
|---------|----------------------------|------------------------------|---|
| 1. | RDX/TNT (60 : 40) | 0.96 | Original acidity of |
| 2. | RDX/TNT/0.5% $CaSiO_3$ | 0.65 | RDX/TNT (60:40) is 0.06% |
| 3. | RDX/TNT 1.0% Zinc Stearate | 0.87 | as HNO_3 |
| 4. | RDX/TNT/5% $CaSiO_3$ | 0.70 | Standard RDX/TNT (60:40) |
| 5. | RDX/TNT/5% Zinc Stearate | 0.92 | Sample was taken to see the compatibility of the additives. |

Note : As per specification RDX/TNT/5% additive should not evolve more than 10 ml gas at 120°C in 40 hours.

This reveals that the additive first reduces the acidity of the composition appreciably and then the unreacted portion of the additive produces alkalinity to the composition superficially. Still the crystals of RDX inside the composition contain a little amount of occluded acidity but well within the acceptable limit and far below the original acidity of the RDX Gr IA, used in the preparation of the composition.

In addition to the study of effect of the additives towards the reduction of the acidity a series of experiments/trials were conducted to assess their behaviour towards other related parameters of the compositions. The results obtained have indicated that the compositions after incorporation of the additives remain unchanged in respect of their sensitivity to impact, friction and electric sparks. Pourability (Flow properties) of the compositions essentially required for filling purposes also does not change. The additives were found compatible with the RDX compositions as shown in Table 5.

To assess the suitability/compatibility of the compositions containing additives with metals (e.g. bomb steel, aluminium, brass, iron, etc.) with which these compositions are supposed to come in contact in regular service use, storage trials (at 50°C for 5 months) were conducted. The observations made are:-

- (i) In case of higher acidity (above 0.05%) in RDX/TNT (60 : 40,) the metal rods get corroded mildly.
- (ii) Alkalinity upto 0.1%, calculated as Na_2CO_3 of the compositions developed due to excess of additive in the compositions did not corrode the metals.

4. Conclusion

Based on the results obtained, in laboratory following conclusions are drawn :-

- (i) 0.5% of Calcium Silicate/1.0% of Zinc Stearate reduce considerably the acidity of RDX/TNT (60 : 40) prepared from RDX containing acidity upto 0.09% as HNO_3 .
- (ii) Direct incorporation of the additives to RDX does not reduce acidity.
- (iii) The reaction of the additives takes place mostly at the time of their incorporation into hot mixture of RDX/TNT (60 : 40).
- (iv) Calcium Silicate and Zinc stearate are compatible with RDX/TNT compositions.
- (v) Storage trials conducted have indicated that RDX/TNT (60 : 40) containing acidity 0.05% as HNO_3 affects/corrodes mildly the metals on storage. Alkalinity upto 0.1% as Na_2CO_3 produced by addition of the additives in the compositions does not have any adverse effect on the metals during storage. This indicates that the alkalinity of the compositions upto 0.1% can be accepted with reference to the maximum acceptable limit of acidity upto 0.05%.
- (vi) Calcium Silicate has been found to be a better additive than Zinc Stearate.

References

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