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1 Aug 1946, PA per document marking; 27 Jun 1968, PA

AD495021

PICATINNY ARSENAL

TECHNICAL GROUP

CHEMICAL DEPARTMENT

TECHNICAL REPORT

SERIAL NO. 1338

DATE 13 September 1943

SUBJECT: DEVELOP PROCESSES FOR THE RECOVERY OF EXPLOSIVE SCRAP

THIRD PROGRESS REPORT

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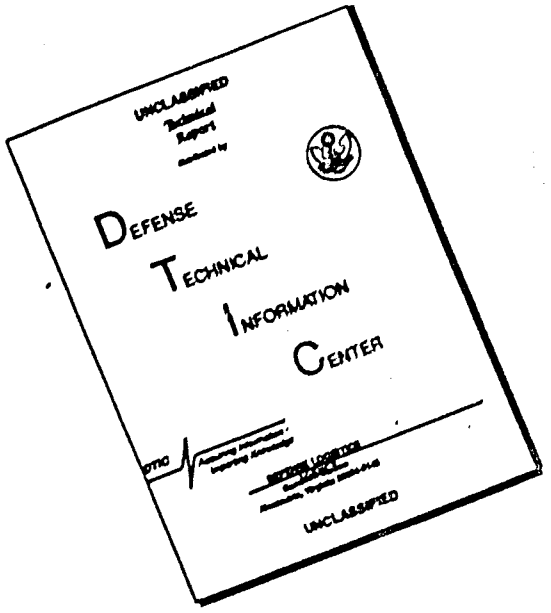

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Picatinny Arsenal
(11) 13 Sept[redacted]43

(12) 15 p.

TECHNICAL REPORT NO. 1338

(6) Develop Processes for the Recovery of Explosive Scrap.

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CLASSIFICATION CANCELLED
BY AUTHORITY OF O. C. M. NO. 30838
[redacted]. CRUMP
DATE 1 AUGUST 1946

msk(282-900)

SYNOPSIS

Since quantities of scrap explosives which may be contaminated with grit or other foreign material are accumulated during loading operations, it would be desirable to have available processes for the recovery of the components of these explosives. RDX is a relatively expensive explosive, and thus, it would be advantageous to recover it from scrap RDX Composition A and RDX Composition B.

Processes have been developed for the recovery of RDX from RDX Composition A and RDX and TNT from RDX Composition B. In the case of RDX Composition A, the wax was extracted by means of benzene. This was accomplished by a batch process and by continuous extraction in a Soxhlet apparatus. The RDX was recovered in satisfactory yields and complied with the applicable specification.

The procedure for RDX Composition B involved extracting the wax with heptane, followed by extraction of the TNT with benzene. This separation was also accomplished by either a batch or a continuous extraction process conducted in a Soxhlet apparatus. The RDX was recovered in suitable yield and complied with the specification requirements. The TNT was recovered in satisfactory yield and complied with the requirements for Grade II TNT. Should the wax be omitted from the RDX Composition B in accordance with a recent recommendation, the extraction with heptane would not be necessary.

It is recommended that the procedures developed in this investigation be studied on a semi-plant scale with both RDX Composition A and RDX Composition B.

Develop Processes for the Recovery
of Explosive Scrap.

INTRODUCTION:

1. In the course of loading operations, quantities of scrap explosive are accumulated which cannot be reused because of possible contamination with grit or other foreign material. It would be advantageous, therefore, to have available methods for the recovery of the components of the compound explosives now in use. Recovery processes for Pentolite and for tetryl-metal stearate scraps have been developed. The procedures used in the recovery of these explosive scraps are described in the first two Progress Reports on this problem (Ref: A and B).

2. Because of the relatively high cost of RDX, recovery methods are desired for use in recovering this explosive from scrap RDX Composition A and RDX Composition B. As in the case of both Pentolite and the tetryl-metal stearate mixtures, the use of a selective solvent appeared to be the most promising type of separation for these RDX explosives.

OBJECT:

3. To determine the solubility of RDX in several inexpensive solvents.

4. To develop procedures for the recovery of RDX from RDX Composition A and for RDX and TNT from RDX Composition B.

RESULTS:

5. The solubility data obtained for RDX are recorded in Table I, along with similar data taken from the literature.

6. The results of the laboratory separations of RDX Composition A are recorded in Tables II and III. RDX complying with specification requirements was recovered when benzene was used to dissolve the wax. The optimum laboratory separation of RDX Composition A involves heating 100 grams of the explosive with 200 cc. of benzene at 70°C., maintaining this temperature for 10 minutes to insure complete solution of the wax, cooling to 50°C. and filtering. The RDX collected on the filter is washed twice with 25 cc. portions of benzene. A yield of 99.8 percent RDX was obtained by this procedure. Residual benzene was removed from the RDX either by drying in an oven at 100°C. or by adding water to the RDX wet with benzene and heating to distill off the benzene. When 50.00 grams of RDX Composition A were extracted in a Soxhlet apparatus with benzene, a yield of 94.1 percent RDX was obtained after 24 siphonings.

7. The results of the laboratory separations of RDX Composition B are given in Tables IV, V, and VI. The process developed involves

extraction of the wax from this composition by means of heptane, followed by extraction of the TNT using benzene. The RDX recovered complied with the specification requirements; the recovered TNT complied with the requirements for Grade II TNT. The separation of RDX and TNT from 200 grams of RDX Composition B was effected by heating the explosive with 800 cc. of heptane at 90°C. for 10 minutes, and then filtering at 85°C. After washing with two 50 cc. portions of heptane the TNT was dissolved in 300 cc. of benzene by heating to 70°C., maintaining this temperature for 10 minutes and filtering. The RDX left on the filter was washed with two 25 cc. portions of benzene. The TNT was recovered from the benzene solution. The recovery of RDX by this process was 99.2 percent of the theoretical and that of TNT was 86.4 percent.

8. The separation of RDX Composition B may also be effected in a Soxhlet apparatus by first extracting with heptane, and secondly, with benzene. In the Soxhlet apparatus from 50.00 gram of RDX Composition B, after 10 siphonings with heptane and 7 with benzene, 94.4 percent of the RDX and 93.2 percent of the TNT was recovered. In several experiments where only the RDX was recovered, and in which the TNT and wax were removed by dissolving in benzene, yields of 97.3 percent of RDX were obtained. In these experiments, 100 grams of RDX Composition B were heated with 150 or 200 cc. of benzene to 70°C., and after holding at this temperature for 10 minutes cooled to either 50°C. or 25°C. and filtered. The RDX, which was collected on the filter, was washed twice with 25 cc. portions of benzene. The residual benzene was removed from the RDX either by drying in an oven at 100°C. or by heating the RDX wet with benzene in the presence of water and steam distilling off the benzene.

DISCUSSION
OF RESULTS:

9. An attempt was made to separate the wax from RDX Composition A by flotation with hot water. Tests showed that the wax remained incorporated with the RDX even when the mixture had been heated to 95°C. These results were not entirely unexpected since a similar procedure is used to prepare the RDX Composition A. This method was tried, however, since it was considered that it might possibly effect the separation at elevated temperatures. In addition, if such a procedure were effective, it would be more economical than one involving the use and recovery of solvents.

10. One possible method for the separation of RDX Composition A might be by the use of a solvent for RDX which did not dissolve the wax. Inspection of the solubilities of RDX in various solvents (Table I) showed acetone to be the only solvent in which RDX is appreciably soluble. Qualitative tests showed that the wax which is incorporated with RDX in RDX Composition A is not appreciably soluble in acetone. On the basis of these facts, an attempt was made to

effect a separation of RDX Composition A by dissolving RDX in acetone, and filtering it free from the wax. Tests showed, however, that the wax clogged the filter, causing the filtration to be extremely slow. Since it was apparent that this approach was impractical, the alternative method of selectively dissolving the wax was tried. Ethyl alcohol was found to be of no value, practically none of the wax being dissolved, even after heating at 70°C. Both benzene and heptane were found to be capable of removing the wax satisfactorily, but with heptane the filtration was quite slow in comparison with benzene. Benzene is an inexpensive solvent ($0.021 per pound) and because of its low boiling point could be easily recovered by distillation.

11. An attempt was made to remove the wax from RDX Composition A using benzene at room temperature, Table II, Expts. 1, 2, and 3. In each case, considerable wax was left in the RDX. It was found necessary to raise the temperature to 70°C. and to maintain this temperature for 10 minutes in order that all the wax might be dissolved. RDX of suitable purity could be obtained when filtration of this mixture was effected at 50°C., but at 25°C. with a greater volume of benzene, some of the wax was not removed from the recovered RDX, Table II, Expts. 4, 5, 6, and 7. Since very little decrease in recovery was noted, Expts. 6 and 7, when 1000 cc. of benzene were used in place of 200 cc. with filtration at 50°C., it is apparent that considerable excess of solvent could be tolerated per unit amount of Composition A without undue loss of RDX.

12. Because a continuous or semi-continuous recovery procedure would be more economical than a batch process, it was thought desirable to investigate the removal of wax from RDX Composition A using benzene in a Soxhlet apparatus. The data obtained in this apparatus should give an indication of the practicability of an extraction process similar to that recommended for the recovery of tetryl-metal stearate scrap and which has been used for tetryl-graphite scrap, Ref. B. It was found, Table III, that although 12 siphonings did not completely remove all the wax, when 24 siphonings were made, a yield of 94.1 percent of RDX complying with the specification requirements was obtained. Undoubtedly on a larger scale, with agitation of the RDX Composition A and benzene, the efficiency of this method of separation could be further improved. Thus, the semi-continuous extraction of RDX Composition A with benzene appears to be a feasible method for the recovery of RDX. It should be noted, Table II, that the melting points of RDX containing wax do not differ substantially from those of RDX from which all wax had been removed. Thus, the melting point of RDX is not a criterion of its freedom from wax; hence, the amount of acetone insoluble material was selected as a measure of purity of this explosive.

13. At present RDX Composition B consists of RDX, TNT, and wax. In order that the wax may be separated from the RDX and TNT a solvent must be used which dissolves neither of these substances, but which

dissolves the wax. It was considered inadvisable to attempt to remove the RDX and TNT from the wax by acetone because of the difficulty experienced in the filtration of the wax from RDX Composition A. Benzene is thus eliminated for this purpose, because it dissolves the TNT as well as the wax. The results of preliminary experiments showed that petroleum ether (hexane) would dissolve the wax. Since, however, the melting point of RDX Composition B, about 80°C., is above the boiling point of hexane, 69°C., there is very little opportunity for the removal of wax from the interior of solid particles of RDX Composition B. Heptane having a boiling point of approximately 98°C., therefore, was tried and was found to be satisfactory. The solubility of TNT in benzene is very large, while that of RDX is very small; thus it appeared logical to use this solvent to separate the TNT from the RDX subsequent to the removal of the wax. This part of the process was also found to be effective. RDX, of satisfactory purity, was recovered in yields of 96.2 percent and 99.2 percent in Expts. 1 and 2, Table V, respectively, despite the varying conditions used. In Expt. 1, 200 cc. of heptane were used and filtration of the heptane solution was made at 50°C.; the benzene extraction was made using 300 cc. of benzene and filtering at 50°C. In Expt. 2, 800 cc. of heptane was used and filtration was conducted at 85°C.; the benzene extraction used 300 cc. of benzene and the filtration were made at 70°C. The TNT recovered complied with the specification requirements for Grade II TNT. For the same reasons, as in the case of RDX Composition A, it was thought advisable to investigate the separation of RDX Composition B in a Soxhlet apparatus. Although 8 heptane siphonings and 4 benzene siphonings, Expt. 1, Table VI, did not completely remove the TNT from the RDX, this was accomplished with 10 heptane siphonings and 7 benzene siphonings, Expt. 2. It is of interest to note that in the heptane extraction in the Soxhlet apparatus, although RDX Composition B became molten, it did not pass through the thimble. If, however, in accordance with a recent recommendation, the wax is omitted from RDX Composition B, it would be unnecessary to include the heptane extraction. Since benzene will dissolve both the wax and the TNT, several experiments were carried out, Table IV, in which the RDX was recovered by benzene extraction of RDX Composition B. In all these experiments, satisfactory yields, 95.7 - 97.3 percent, of RDX were obtained.

14. In the recovery of RDX from both RDX Composition A and RDX Composition B, it is necessary to consider the separation of the explosive from grit which may be present. This could be accomplished by dissolving the RDX, retained on the filter, in acetone, and then precipitating it from the acetone solution by the addition of water. If acetone extraction was applied to RDX wet with benzene, a quantity of benzene would be lost with every batch. If the benzene could be displaced with water, then the benzene could be recovered and this explosive would be left wet with water. Experiment showed, however, that the benzene was not displaced when water was added to a slurry of RDX and benzene. Instead, a pasty mixture of RDX, benzene, and water was formed. Variations in the quantities of benzene and water and the

addition of salt did not alter this result. RDX was finally obtained in crystalline form from the water-benzene mixture by raising the temperature and steam distilling the benzene. In the laboratory experiments the benzene began to steam distill at 70°C. This process was applied to RDX recovered from both RDX Composition A, Table II, Expts. 8 and 9, and RDX Composition B, Table IV, Expt. 5. In each case the RDX so obtained complied with the specification requirements and thus could be reused. It would be possible, therefore, to effect removal of residual benzene by adding water to the benzene-wet RDX and steam distilling. The benzene can be recovered from the distillate. The majority of the water could then be siphoned from the RDX and the acetone process applied to the explosive wet with water. The TNT recovered from RDX Composition B, which complied with the requirements for Grade II TNT, is probably contaminated chiefly with RDX; it could be reused for the manufacture of RDX Composition B, or for any purpose for which Grade II TNT is acceptable.

CONCLUSIONS:

15. It is concluded that RDX may be recovered in satisfactory yield and purity from RDX Composition A by the use of benzene to dissolve the wax.

16. It is concluded that good yields of RDX complying with the specification requirements may be obtained from RDX Composition B by first extracting the wax with heptane and subsequently extracting the TNT with benzene. The TNT, which is recovered in satisfactory yield, complies with the specification requirements for Grade II TNT.

RECOMMENDATIONS:

17. It is recommended that a semi-plant study of the recovery of RDX from RDX Composition A be made using the process described in this report. In the semi-plant study the following procedure should be used.

a. Extract the scrap RDX Composition A with sufficient benzene to remove the wax. The RDX should then be washed with benzene. The benzene used in these operations may be recovered from the wax by ordinary distillation or by steam distillation.

b. Add water to the RDX wet with benzene and heat the mixture so as to steam distill the benzene. Collect the distillate and recover the benzene.

c. Remove the greater portion of the water from the RDX and add acetone to dissolve it. Filter the acetone solution to remove any grit and add water to precipitate the explosive. The acetone can be recovered by distillation from the water solution with rectification. It is possible that this phase of the process could be conducted in a manner similar to that used in the recovery of tetryl from tetryl containing graphite.

18. It is recommended that a semi-plant study of the recovery of RDX and TNT from scrap RDX Composition B be made using the process described in this report. The procedure for recovering the RDX is to be the same as that given above for RDX Composition A. Recover the TNT, which is removed in benzene solution from the RDX by steam distilling the benzene solution. The benzene collected from this distillation may be reused. Should wax be present in the RDX Composition B, it can be removed by extracting the explosive with heptane prior to the benzene extraction.

EXPERIMENTAL

PROCEDURE:

19. In the extractions, other than those with the Soxhlet apparatus, a definite volume of solvent (benzene or heptane) was added to a definite weight of either RDX Composition A or RDX Composition B. The mixtures were heated to a definite temperature, maintained there for 10 minutes in order that solubility equilibrium might be attained and after cooling to a definite temperature, filtered. The material retained on the filter was washed twice with definite portions of solvent. In the case of TNT recovery from RDX Composition B, the benzene filtrate was evaporated to obtain the TNT.

REFERENCES:

A. Technical Report No. 1284.
B. Technical Report No. 1287.
C. Technical Report No. 1313.

Table I

Solubility of RDX in Various Solvents
(gms. RDX per 100 gms. solvent).

Temperature, °C.	20	30	39	40	50	52	60	70
Solvent								
Benzene[a]	0.045	0.055		0.085	0.115		0.195	0.300
Toluene[a]	0.020	0.025		0.050	0.085		0.125	0.210
Chlorobenzene[b]	0.33					0.78		
Trichloroethylene[b]	0.20					0.23		
Tetrachloroethane[b]			0.09					
Carbon tetrachloride[a]					0.005		0.007	0.015
Methyl alcohol[a]	0.235	0.325		0.480	0.735		1.060	
Ethyl alcohol[a]	0.105	0.155		0.235	0.370		0.575	0.880
Isopropyl alcohol[b]			0.19					
Isobutyl alcohol[b]	0.08							
Isoamyl alcohol[a]	0.026	0.040		0.060	0.110		0.210	0.320
Acetone[a]	6.81	8.38		10.34	12.80			
Methyl acetate[b]	2.95		4.01			6.06		
Ethyl acetate[a]	0.055	0.075						
β ethoxy ethyl acetate[b]	1.47		1.88			2.65		

[a] Urbanski and Kwiatkowski in Seidell, Solubilities of Organic Compounds, 3rd. Ed. Vol. 2, p. 196.
[b] Determined during this investigation.

Table II

Recovery of RDX Composition A Using Benzene[a]

Expt. No.	Highest temp. to which Comp. A and benzene were heated, °C.	Temp. of filtration, °C.	Volume of Solvent, cc.	Grams of benzene insol. (RDX)	Grams Undissolved wax per 100 gm. Comp. A	Melting point of RDX, °C.	Remarks
1	25	25	200	92.2	1.8	-	Six hours contact of benzene and Comp. A.
2	25	25	250	93.5	3.1	203	Stirred for 1 hour.
3	25	25	300	93.0	2.6	204	Stirred for 3½ hours.
4	70	25	200	93.3	2.9	-	At 70°C. for 10 min.
5	70	25	250	91.5	1.1	203	" " " " "
6	70	50	200	90.2	-	204	" " " " "
7	70	50	1000	89.1	-	204.6	" " " " "
8[b]	70	50	800	88.0	-	200.5	" " " " "
9[b]	70	50	400	88.0	-	200.5	" " " " "

[a] All experiments were made using 100 gm. samples of RDX Composition A with an analysis of 90.4 percent RDX and 9.6 percent wax.

[b] In these two experiments the residual benzene was removed by heating in the presence of water until the benzene had been entirely steam distilled. The acetone insoluble in the recovered RDX was 0.04 and 0.02 respectively; the acidity in both samples was nil. These samples of RDX thus comply with the requirements of Specification AXS-745.

PA Tech.Report No. 1338
13 September 1943

Table III

Recovery of RDX from RDX Composition A
Using Benzene in a Soxhlet Apparatus[a]

Expt. No.	No. of siphonings	Weight of RDX recovered, gms.	Percent of RDX recovered	Melting[b] point of recovered RDX, °C.	Acetone[b] insoluble in recovered RDX, %
1	5	46.0	101.8	-	-
2	12	44.4	98.3	203	0.46
3	24	42.5	94.1	204	0.04

[a] In these experiments 50.00 gm. samples of RDX Composition A were used; the analysis of the RDX Composition A was 90.4 percent RDX and 9.6 percent wax.

[b] RDX specification requirements:

Melting point, Type A	200°C., minimum.
Acetone insoluble	0.05%, maximum.

Table IV

Recovery of RDX from RDX Composition B Using Benzene[a]

Expt. No.	Highest temp. to which Comp. B and benzene were heated, °C.	Temp. of filtration, °C.	Volume of Solvent, cc.	Yield of RDX, grams	Yield of RDX, %	Melting point RDX, °C.
1	70	25	150	59.0	95.7	198.0
2	70	25	150	60.0	97.3	198.5
3	70	25	200	60.0	97.3	198.5
4	70	50	150	60.0	97.3	198.5
5[b]	70	50	400	59.0	95.7	197.0

[a] In all experiments 100 gm. RDX Composition B were used which contained 61.7 percent RDX.

[b] In this experiment the residual benzene was removed from the RDX by heating in the presence of water. The acetone insoluble matter of the recovered RDX was 0.05 percent and the acidity was nil, thus complying with the requirements of Specification AXS-745.

PA Tech.Report No. 1338
13 September 1943

Table V

Recovery of RDX and TNT from RDX Composition B Using Heptane and Benzene[a]

	Experiment No. 1	Experiment No. 2	Specification Requirement
Heptane extraction:			
Highest temp., °C.	90	90	
Filtration temp., °C.	50	85	
Volume heptane, cc.	200	800	
Benzene extraction:			
Highest temp., °C.	70	70	
Filtration temp., °C.	50	70	
Volume benzene, cc.	300	300	
Yield, RDX, %	98.9	99.2	
Melting point, RDX, °C.	196.6	195.0	Type B, 190 minimum
Acetone insoluble in RDX, %	0.03	0.02	0.05 maximum
Yield, TNT, %	102.1	86.4	
Setting point, TNT, °C.	79.8	79.37	Grade II, 76.0 minimum
Alcohol insoluble in TNT, %	0.05	0.00	0.05 maximum

[a]In these experiments, 200 gm. samples of RDX Composition B were used; the composition of the RDX Composition B was: 61.7 percent RDX, 36.8 percent TNT, and 1.5 percent wax.

Table VI

Recovery of RDX and TNT from RDX Composition B Using Heptane and Benzene in a Soxhlet Apparatus[a]

Expt. No.	No. of heptane siphonings	No. of benzene siphonings	RDX recovered, gms.	RDX recovered, %	TNT recovered, gms.	TNT recovered, %
1	8	4	31.9	105.2[b]	15.7	81.7
2	10	7	28.6	94.4	17.9	93.2

[a]In these experiments 50.00 gm. samples of RDX Composition B were used; the composition of the RDX Composition B was: 60.6 percent RDX, 38.4 percent TNT, and 1.0 percent wax.
[b]Evidently not all the TNT or wax had been removed from the RDX.