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RECOVERY OF ORGANIC VALUES FROM TNT MANUFACTURING WASTES

EVERETT E. GILBERT

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
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Pure 2,4 DNT-3- and -5-SO_3Na were prepared from 2,3,4- and 2,4,5-TNT, respectively, and a procedure was developed for their extraction (as a mixture) from red water. Reactions of the sulfonates were studied, with special emphasis on direct and indirect methods for desulfonating them to 2,4-DNT. Reactions studied also included reduction of the nitro groups, followed by desulfonation to 2,4-DAT; heating with sulfur dioxide (giving 2-amino-4-nitrotoluene by partial reduction and desulfonation); and replacement of the sulfonate group by

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20. ABSTRACT (Contd)

chlorine, hydroxyl. sulfur, cyano, and various substituted amino groups. Most of these reactions with pure sulfonates were also applied to the corresponding TNT isomers, and in some cases directly to red water. The economic feasibility of 2,4-DAT recovery was considered.

Also discussed were recent studies on the recovery of TNM from TNT process gas, and the recovery of TNB from TNT oxidation products.

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INTRODUCTION

The production of TNT entails notable problems of air and water pollution. In the former category is the formation of the hazardous and toxic compound TNM, about 0.4 ton of which is formed by side reactions per 100 tons of TNT. By order of the Environmental Protection Agency, this material can no longer be vented to the atmosphere. Water pollution occurs during purification of the crude TNT with aqueous sodium sulfite (sellite), during which about 4 tons of TNT by-product isomers, per 100 tons of crude TNT, are converted to DNT sulfonates, and discarded in the waste "red water". In addition, TNT oxidation products, such as PiCOOH, are formed in small amounts.

In the case of TNM, what is required is development of a recovery procedure, since it already has uses in the production of several energetic plasticizers (e.g. bis (2-fluoro-2,2-dinitroethyl) formal (FEFO)). Recoverable TNT oxidation products can easily be converted by known methods to TNB, a useful explosive. The DNT sulfonates, on the other hand, have no current uses - either as such or as known derivatives.

The objective of this program was to develop methods for the recovery of TNT by-products (TNM, DNT sulfonates, oxidation products) in usable form, thereby possibly obtaining financial credit for the process, as well as reducing pollution.

As indicated more specifically below, the work reported herein was done at the Naval Surface Weapons Center (White Oak), Silver Spring, MD; Radford Army Ammunition Plant (RAAP), Radford, VA; and Picatinny Arsenal (now Energetic Materials Division, Large Caliber Weapon Systems Laboratory (LCWSL, ARRADCOM), Dover, NJ.

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RESULTS AND DISCUSSION

TNM Recovery Studies

In late 1972, funds were provided by the Explosives Division, Picatinny Arsenal to the Naval Ordnance Laboratory for a study of the recovery of TNM from TNT process exit gas (Ref 1). This work resulted in the development of two efficient procedures for doing this, involving the use of aqueous alkali with hydrogen peroxide, or of aqueous alkali with a long-chain alcohol (Ref 2). Further study of these methods at RAAP (Ref 3,4) indicated that the alkali-hydrogen peroxide system gave economically feasible recovery of TNM as sodium nitroformate, based on the cost of the chemicals required.

Work was discontinued at the end of FY76 on this promising process for the following reasons: (1) the quantity of nitroform obtainable might be insufficient for potential requirements (2) the capital cost of a recovery unit would be high (3) the EPA requirement that TNM not be vented to the atmosphere is easily satisfied by its destruction with sellite.

DNT Sulfonate Recovery Studies

The objectives of this portion of the program were as follows:

1. Prepare pure 2,4-DNT-3- and -5-SO_3Na.

2. Study their reactions as a basis for their recovery from red water and their conversion to potentially useful derivatives.

3. Try reactions found promising with the pure sulfonates directly with red water.

4. Develop a practical method for isolating the sulfonates from red water.

The work described below was done at the Explosives Division, Feltman Research Laboratory, Picatinny Arsenal.

Preparation of Pure Model Sulfonate - Initial work on all projected approaches for recovery of the DNT sulfonates was done with the pure compounds. 2,4-DNT-5-SO_3Na was prepared from 2,4,5-TNT and aqueous sodium sulfite essentially by the method of Brady et al. (Ref 5). The analogous 3-SO_3Na was made similarly from 2,3,4-TNT by the method of Gornall et al. (Ref 6). Details of both procedures are given in Appendix A, and reference is made there to the isolation of an explosive by-product by acidification of the residual mother liquor from the preparation of 2,4-DNT-5-SO_3Na. The required 2,4,5- and 2,3,4-TNT isomers were prepared by the improved method described by Dennis et al (Ref 7), involving the nitration of 3,4- and 2,3-DNT, respectively. During the course of this study, those DNT isomers became commercially unavailable. A simplified procedure for their preparation was, therefore, developed, starting from the available corresponding nitrotoluidines (Ref 8). 2,4-DNT-5-SO_3Na has also been made (Ref 9) by an alternative method from 3-chlorotoluene, involving dinitration to 2,4-dinitro-5-chlorotoluene, conversion of the latter to bis(2,4-dinitro-5-methylphenyl) disulfide, and oxidation to the desired sulfonic acid. An attempt to prepare the analogous 3-SO_3Na by this method was unsuccessful at the last step.

Study of the Reactions of the Sulfonates - In contrast to the fairly extensive work on the reactions of the TNT isomers (Ref 5,6, 10,11,12,13), very little work has been done on the reactions of the 2,4-DNT sulfonates. Muraour (Ref 10) reports that 5-SO_3Na reacts with ammonia to form the corresponding dinitrotoluidine, but gives no details. Brady et al. (Ref 5) state that ammonia does not "readily" react with it, but that methylamine forms the corresponding substituted toluidine; no details are given. A British report (Ref 14) states that both sulfonate isomers react with methylamine to give the corresponding substituted toluidines, and proposes their nitration to "methyl tetryl" as a method for red water utilization. No details are given, and it is not clear whether this approach was actually demonstrated with red water. Dennis et al. (Ref 9) showed that methylamine reacts easily with 5-SO_3Na to give a good yield of product. They also showed that reductive desulfonation of the same isomer to 2,4-DNT is effected in 5% yield with sodium borohydride. Several unsuccessful attempts were made to effect hydrolytic desulfonation of 5-SO_3Na to 2,4-DNT by boiling with aqueous mineral acids (Ref 5,15,16) at atmospheric pressure. Aside from the experiment with methylamine cited above, work on the less accessob;e 3-SO_3Na has been limited to reduction of the nitro to amino groups and oxideation of the methyl group to carboxyl (Ref 6).

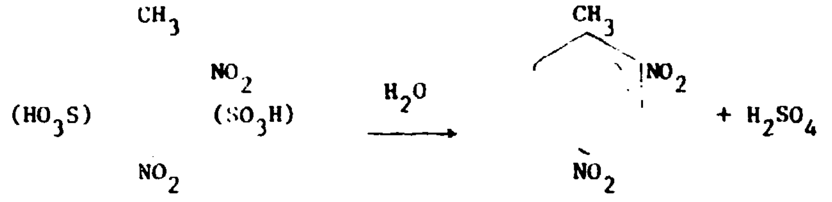
An objective of this program was, therefore, to supplement these very limited and fragmentary studies toward obtaining a more complete understanding of the chemical behavior of the sulfonates, which in turn can provide a basis for their rational recovery and/or utilization.

Desulfonation to 2,4-DNT - Procedures for the conversion of both 2,4-DNT sulfonates back to 2,4-DNT (Reaction 1) are of obvious interest because the DNT can be recycled to the nitration process, thereby increasing the yield of the 2,4,6-isomer. Several "direct" and "indirect" methods for doing this have been considered, as follows:

Direct Desulfonation Approaches - Hydrolytic Desulfonation

Thermal

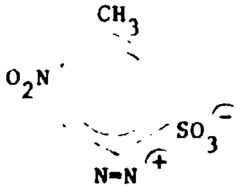
Many types of aromatic sulfonic acids can be desulfonated by heating in aqueous acid medium (Ref 17). This is a general reaction which has been widely used for research and industrial purposes. Application of it to the two sulfonates present in red water would yield only 2,4-DNT, as follows:



2,4-DNT

(1)

Unfortunately, nitroaromatic sulfonic acids resist desulfonation. Vesely and Stojanova (Ref 15) reported that 2-, 3-, and 4-nitrobenzenesulfonic acids do not desulfonate in phosphoric acid. They give no details for these experiments, but did obtain satisfactory desulfonation with a series of 15 other sulfonic acids, including benzenesulfonic acid at 227°C. Brady et al. (Ref 5), referring to 2,4-DNT-3- and -5-SO_3H, say that "all attempts to remove the sulfo group by hydrolysis, with production of the dinitrotoluenes, have been unsuccessful", but give no details. No reaction was noted upon heating 2,4-DNT-5-SO_3H with aqueous sulfuric or phosphoric acids in the range 130-150°C (Ref 16), in a study made recently at RAAP. No 2,4-DNT was noted from heating spent sellite with phosphoric acid at 150°C (Ref 18) and, in one of these experiments, a violent explosion occurred. A compound exploding at 145°C was recently isolated at PA upon acidification of the filtrate from a preparation of 2,4-DNT-5-SO_3Na from 2,4,5-TNT and sodium sulfite (cf. experimental data in Appendix A) (Ref 762-387-34)*. This compound is thought to have the structure given below (Ref 19).



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*Refers to item in author's research notebook.

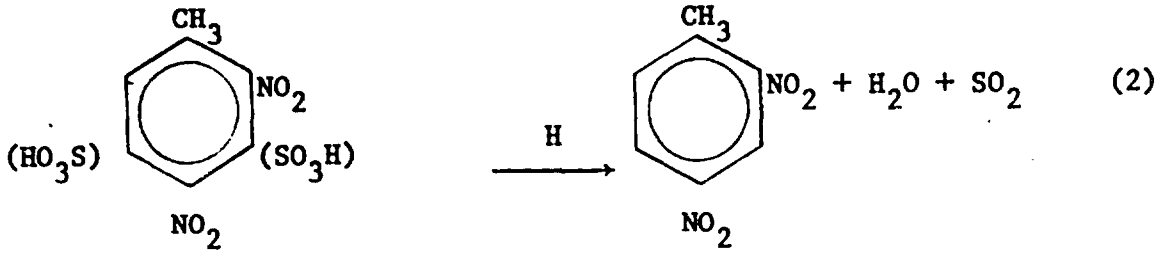
It evidently results from the reduction and diazotization of the 4-nitro group in 2,4-DNT-5-SO_3Na; NO_x formation was indeed noted during isolation of the compound at PA. Since the compound is water-insoluble, it should be removed by filtration from acidified red water before the solution is heated. It is noteworthy that the explosive solid was not obtained by the acidification of another preparative run made at room temperature instead of the usual 60-65°C; 5-hydroxy-2,4-DNT was precipitated, however (cf. Appendix A). It is also noteworthy that the explosive compound was not precipitated by the acidification of stabilized Joliet red water (Ref 762-387-34). It thus appears that the conditions of sulfite treatment determine whether or not the explosive precursor is formed.

A series of 8 runs was made in this study attempting to desulfonate 4-nitro-, 2,4-dinitro-, and 2,4,6-trinitrobenzene-sulfonic acids in phosphoric and trifluoromethanesulfonic acids. These runs were made at atmospheric pressure at temperatures as high as 300°C. No desulfonation was noted in any case, even though the expected results were obtained in blank experiments with other sulfonic acids. The effectiveness of trifluoromethanesulfonic acid for desulfonation in general was first noted in the present study (Ref 20). (Ref 762-183-101; 762-221-6,18,73,97).

A series of 5 experiments was then run with 2,4-DNT-5-SO_3Na in 30-43% H_3PO_4 in a pressure vessel at 200° for 1-5 hours. Under the milder conditions, no reaction occurred, but under the more stringent conditions only decomposition was noted, as indicated by charring and SO_2 evolution. It is therefore concluded that thermal hydrolytic desulfonation is not a promising approach (Ref 762-352-64,70).

<u>Photochemical</u> - The recent literature indicates that hydrolytic desulfonation (Equation 1) can be photochemically activated in certain cases. Although preliminary efforts to desulfonate 2,4-DNT-5-SO_3Na were unsuccessful, this approach is considered worth further study (Ref 762-276-63 (Dr. S. Bulusu)).

<u>Reductive Desulfonation</u> - Reductive desulfonation involves the following reaction:



(2)

2,4-DNT

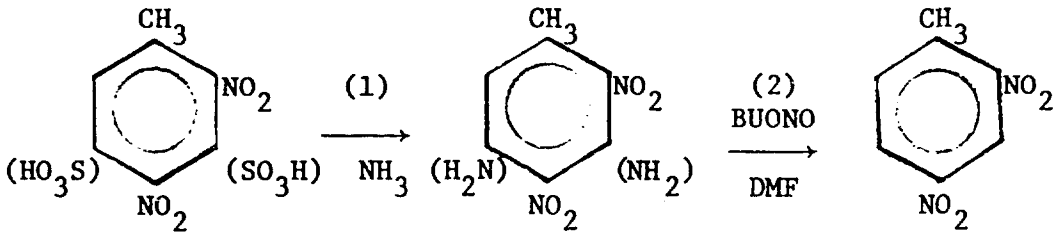
Dennis et al. (Ref 9) obtained a 5.5% yield of 2,4-DNT upon treatment of the 5-SO_3Na in one run with $NaBH_4$. This reaction was not studied further.

The reductive desulfonation of 2,4,6-trinitrobenzenesulfonic acid to TNB, using N-benzyldihydronicotinamide at room temperature, has been recently reported (Ref 21). Conversion of 2,6-dinitrobenzenesulfonic acid to 1,3-DNB by this procedure has also been noted (Ref 22), although the reaction was greatly hampered by the lack of a third negative substituent on the ring. We have confirmed this preparation of TNB from the sulfonic acid, but have obtained negative results with 2,4-DNB-SO_3Na and with 2,4-DNT-5-SO_3Na (Ref 762-387-65,67,73,74,76). Similar results were obtained with N-ethyldihydronicotinamide (Ref 762-387-97,98). It thus appears that desulfonation methods are available for electropositive aromatic rings and for highly electronegative aromatic rings, but none are as yet known for rings of intermediate electronegativity, i.e., with two nitro groups, except for the one case cited above.

Indirect Desulfonation Methods

Via 3- and 5-Amino-2,4-DNT

This concept involves the following reactions:



(3)

2,4-DNT

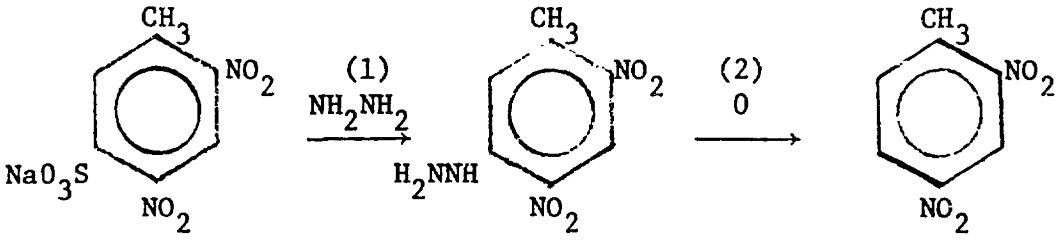
As noted subsequently, a mixture of amino DNT isomers can be obtained easily by heating stabilized red water with ammonia under pressure (Reaction 3-1); the mixture was isolated in good purity by simple filtration.

Reaction 3-2 gave a 72% yield of 2,4-DNT from 5-amino-2,4-DNT; the 3-amino isomer was not studied (Ref: 762-316-29).

The above results show that the concept of converting red water sulfonates to 2,4-DNT *via* the amines is feasible. For such an approach to be economical, however, the yields in both steps require considerable improvement, and a cheaper reagent system would be needed for the second step.

Via 5-Hydrazine-2,4-DNT

As detailed subsequently, the following new reaction 4-1 was noted:



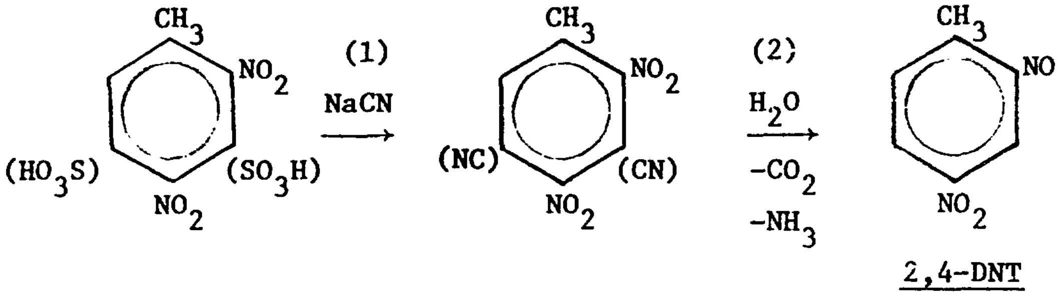
(4)

2,4-DNT

Reaction 4-2, a known type of reaction, was used to convert the hydrazine compound to 2,4-DNT. Sequence 4 is of no economic interest, however, because of the high price of hydrazine and the low yield in Reaction 4-2 (Ref 762-387-6).

Via 3- and 5-Cyano-2,4-DNT

The following sequence was visualized as feasible:



(5)

Reaction 5-1 is unknown, but 5-2 is a known type. Unsuccessful attempts were made to effect Reaction 5-1 using KCN or $Ba(CN)_2$ in DMF with the model compound 2,4-DNB-SO_3Na. Similar unsuccessful efforts were made to replace the 5-nitro group in 2,4,5-TNT; a 58% yield of 2,4-dinitro-5-hydroxytoluene was obtained instead (Ref 762-268-38,99; 762-241-10; 762-316-37). Efforts to effect these reactions photochemically were also fruitless (Ref 762-276-29,31-39 (Dr. S. Bulusu)).

Via 3- and 5-Chloro-2,4-DNT

The following reaction is known, when R is 2,4,6-trinitrophenyl (Ref 23), and 2,4-dinitrophenyl (Ref 24):

$$RSO_3H + POCl_3 \rightarrow RCl \qquad (6)$$

We have found that 2,4-DNT-5-SO_3Na can be converted to 5-chloro-2,4-DNT in 84% crude yield by this procedure (Ref 762-405-6). Under the same conditions, 2,4-DNT-3-SO_3Na gave the corresponding sulfonyl chloride, RSO_2Cl, rather than the desired compound 3-chloro-2,4-DNT (Ref 762-405-7). 5-Chloro-2,4-DNT was also prepared by reacting 2,4,5-TNT with $POCl_3$, a reaction reported in the literature (Ref 24) (Ref 762-405-11). We have also made 3-chloro-2,4-DNT by this procedure from 2,3,4-TNT for the first time (Ref 762-405-12). The reactions involved are:

$$\mathrm{RNO_2 + POCl_3 \rightarrow RCl + NO_x} \qquad (7)$$

Efforts to convert 3-chlorosulfonyl- to 3-chloro-2,4-DNT, by heating were unsuccessful (Ref 762-405-10). This is a known type of reaction:

$$\mathrm{RSO_2Cl \xrightarrow{Heat} RCl + SO_2} \qquad (8)$$

The replacement of chlorine by hydrogen in aromatic nitrochloro compounds is also known (Ref 25):

$$\mathrm{RCl \xrightarrow[RCOOH]{Cu} RH} \qquad (9)$$

We have applied this approach to the conversion of 3- and 5-chloro-2,4-DNT to 2,4-DNT (Ref 762-405-17,18). Adding Equations 6 and 9, in the case of 2,4-DNT-5-SO_3Na, we have:

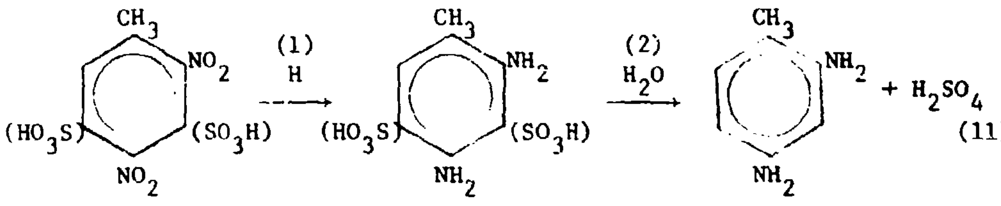
$$\text{2,4-DNT-5-SO}_3\text{Na} \xrightarrow{\text{(1) POCl}_3 \;\text{(2) Cu}} \text{2,4-DNT} \qquad (10)$$

This method is not of economic interest because of reagent costs and our inability to apply it to 2,4-DNT-3-SO_3Na.

Reduction Followed by Desulfonation

Conversion to 2,4-DAT

This concept involves the following reactions:



(11)

2,4-DAT

This approach appeared of interest because no difficulty was envisaged in disposing of the 2,4-DAT via the existing large commercial market for polyurethane resins. In addition, step 11-1 is a widely used type of commercial reaction.

Catalytic hydrogenation of the model compound 2,4-DNB-SO_3Na in aqueous solution gave the predicted hydrogen uptake (Ref 762-247-70). A commercial source (Ref 26) has indicated, however, that catalyst life is usually short when hydrogenating impure nitro compounds, or mixtures thereof. Reduction of 2,4-DNT-5-SO_3Na with iron and HCl gave a 60-75% yield of 2,4-DAT-5-SO_3Na, but reaction with iron and sulfuric acid gave reduction of the 2-nitro group only. Direct reduction of red water with iron and HCl gave a 40% yield of DAT sulfonates (Ref 762-316-72, 74).

Reaction 11-2 was carried out by refluxing DAT sulfonic acid with 65% sulfuric acid for 7 hours at 148-155°C. The solution was cooled, crystallized, and filtered to recover the sulfate of 2,4-DAT. The filtrate acid was refortified with fresh 65% acid and the cycle was repeated. This was done four times, and presumably several additional recycles are possible. The yield of 2,4-DAT was 90% (Ref 762-247-20 and 27). A report was made on the recovery of 2,4-DAT from red water by this approach (Ref 27).

An informal economic analysis, assuming 88 and 90% yields in reactions 11-1 and 11-2, respectively, did not appear promising because of high labor and overhead (Ref 28). Details are given in Appendix B.

Use of Sulfur Dioxide - It was thought that a simplified, "one-pot" approach to reduction-desulfonation via sequence 11 might be effected by heating the 2,4-DNT sulfonates with aqueous sulfur dioxide under pressure. This would eliminate the hydrogenation step, since the nitro groups would be reduced to amino by the sulfur dioxide, which would be converted thereby to sulfuric acid. The acid would then catalyze defulfonation to 2,4-DAT.

To test this concept, 2,4-DNB-SO_3Na was heated 3 hours at 215°C under pressure with 6% aqueous sulfur dioxide. A solid product was obtained, identified as 3-nitroaniline, in 29% yield. (Ref 762-316-28(Run 12)). This compound is evidently formed by partial reduction and and defulfonation.

This experiment was repeated with 2,4-DNT-5-SO_3Na for 3 hours at 180°C. It was found that 31% was converted to 2-amino-4-nitrotoluene, 35% of the starting compound was recovered, and 34% was unaccounted for (Ref 762-316-57 (Run 4)). A similar test with 2,4-DNT-3-SO_3Na gave a 29% yield of 2-amino-4-nitrotoluene (Ref 762-405-22).

Tests were run with Joliet stabilized red water, which was saturated with SO_2 gas at 10°C, followed by heating 3 hours at 180°C under pressure. The yield of 2-amino-4-nitrotoluene was 43% based on the reacted sulfonates, and some of the latter was recovered unchanged. Similar yields were obtained at 165°C for 3 hours (Ref 762-405-25).

These results are considered encouraging. It is felt that further study, especially using more concentrated solutions of SO_2, may give 2,4-DAT as the product, and that complete conversion of the sulfonates may be achieved.

Reaction with Amino Compounds - As noted above, the literature reports that methylamine reacts with both sulfonates, and that ammonia reacts with 5-SO_3Na. This reaction was extended in the present study to the use of hydrazine, and various aliphatic and aromatic amines. Initial work was done with the pure sulfonate isomers preliminary to the direct use of direct water.

Amino Compounds with Pure Sulfonate Isomers - The data are summarized in Table 1. In all cases, the reaction occurring is typified by Reaction 3-1, in which the sulfonate group is replaced by RNH-, R being H (in the case of ammonia), NH_2 (for hydrazine - Reaction 4-1), or organic (in the case of amines). The same derivative was also always prepared independently from 2,3,4-or 2,4,5-TNT. As noted in Table 1, several of these derivatives are new compounds.

It is noted that 5-SO_3Na usually forms the 5-amino derivative in fair to good yield, except for morpholine, the only secondary amine tried other than dimethylamine. Aniline required drastic reaction conditions.

On the other hand, 3-SO_3Na showed little or no reaction with hydrazine or dimethylamine, and often gave lower yields than 5-SO_3Na with other amines. This may be explained by greater steric hindrance in 3-SO_3Na.

It thus appears that facile reaction with both isomers is limited to ammonia and the primary aliphatic amines, with ammonia reacting less easily than the amines. It is of interest that the sulfonates react much less easily than the corresponding TNT isomers to form the same products. This is especially pronounced with amines of low basicity, i.e. aniline. Dennis and Rosenblatt (Ref 9) noted that the rate constant for the reaction of methylamine with 5-SO$_3$Na is 250 times less than that with 2,4,5-TNT.

The reaction with ammonia was first tested with the benzene analogue 2,4-DNB-SO$_3$Na. In a series of 16 runs, it was heated with ammonium hydroxide under various conditions, including reaction in a pressure bottle to avoid loss of ammonia. In all cases, the expected 2,4-dinitroaniline was obtained. In initial runs, the maximum yield was about 70%. However, the yield rose to nearly quantitative upon the addition of BaCl$_2$ to fix the liberated sulfite ion (Ref 762-268-95).

The ammonia reaction was then tried with 2,4-DNT-5-SO$_3$Na. This reaction was run in a pressure bottle by heating 1 hour at 90°C with 30% ammonium hydroxide. In a series of 6 runs, the best yields using added BaCl$_2$ were 75-85% (Ref 762-316-27). 2,4-DNT-3-SO$_3$Na gave a 36% of 3-amino-2,4-DNT using a procedure which gave 59% with the 5-SO$_3$Na and 72% with 2,4-DNB-SO$_3$Na (Ref 762-316-36).

The reaction of hydrazine with aromatic sulfonates is apparently novel, and is quite specific. 2,4-DNT-5-SO$_3$Na and 2,4-DNB-SO$_3$Na both react to give the hydrazino derivatives, but the former does not react with phenylhydrazine, 1,1-dimethylhydrazine, hydroxylamine or guanidine. Hydrazine does not react with 2,4-DNT3-SO$_3$Na in appreciable yield, and not at all with 4-nitrobenzenesulfonic acid (Ref 762-352-95 to 100; 762-387-87 to 89).

Amino Compounds with Stabilized Red Water - With the studies using pure sulfonate isomers as a background, the same amino compounds were reacted directly with stabilized Joliet AAP red water.

The preparation and analysis of the stabilized red water is described in detail elsewhere (Ref 29). In was stabilized by acidification to pH 3.7 (from an initial pH 8.4) with 25% sulfuric acid, allowed to stand for a week, and filtered. The filtrate was then extracted successively with benzene and ether. The total of filtered solid and the two extracts was 0.47% of the weight of the red water, and the major constituent was alpha-TNT. Analysis of the treated red water showed the following:

Inorganics	5-8%
DNT Sulfonates	4.5%
Red Tar	8.4%
Total	18-21%

As discussed more fully below, the red tar comprises organic sulfonates derived from alpha-TNT under drastic conditions of selliting (Ref 29). It was anticipated that it might seriously interfere with attempts to isolate reasonably pure products by reaction of amino compounds with the sulfonates also in the red water. It was found, however, that in most cases the desired products could be obtained in good yield and purity.

The runs were made at 25° and 95°C, using a large excess of amino compound in all cases. The products from ammonia, hydrazine, methylamine, dimethylamine and isopropylamine were all solids easily recoverable by simple filtration of the reaction mixture. The products from n-butylamine, isobutylamine, n-dodecylamine and cyclohexylamine were semi-solid, being mixtures of the solid 5-isomer and the oily (or low-melting) 3-isomer. These were best isolated by cooling the reaction mixture, decanting the residual red water from the semi-solid product, and washing the product with fresh water by decantation. The product was next taken up in chloroform, filtered if necessary, and water washed. It was then recovered as a deep red, semi-solid by evaporation of the solvent.

The results are summarized in Table 2. In general it is noted that they are similar to those obtained with the pure sulfonates. Morpholine and aniline give very low yields, while hydrazine and dimethylamine react only with 5-SO_3Na. Ammonia is unique in giving no product at 25°C, while methylamine and dimethylamine give the same yields at both temperatures. Use of the higher temperature is undesirable with hydrazine, but with the other compounds gives a good yield as opposed to a low one at 25°C. Several of the amines (methyl, isopropyl, n-butyl, isobutyl, and cyclohexyl) gave products with isomer ratios close to those of the sulfonates in the red water, showing that both isomers react completely. As stated above, the amino compounds were always used in large excess. In the case of ammonia and hydrazine, the yields declined if the amount of excess reagent was reduced; this was not studied with the other compounds. This point should be addressed in any further work, as should also ease of recovery of excess reagent. Use of more concentrated solutions obtained by partial evaporation of the red water should also be studied.

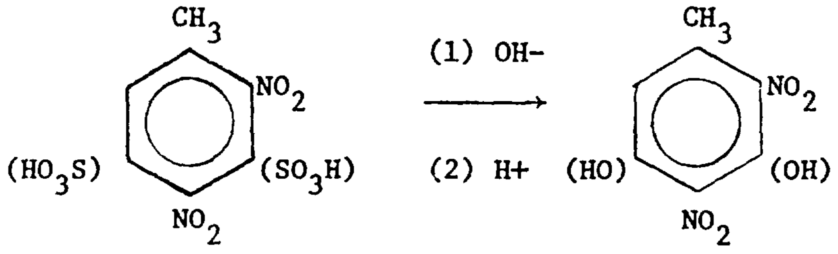
Possible Uses of the Amino Derivatives - The above results show that the mixed isomeric products can be obtained fairly easily in quantities ranging from about 1.5 to 5 pounds per 100 pounds crude TNT, depending upon the amine used. This corresponds to 1500 to 5000 pounds per TNT line per 24 hour day. It seems possible that raw red water could be used at the plant, rather than the stabilized material employed in this study. What possible uses are there for these materials? The fact that mixtures are obtained in most cases is an objection to their use as chemical intermediates. However, the mixed isomers yield only one product upon nitration, and upon replacement of the amino function by H. The nitration concept was proposed many years ago, based on the easily-available methylamine derivative (Ref 14). This approach gives "3-methyl tetryl", an explosive which has apparently not been developed for use. Replacement of the amino group by H in the mixed isomers derived from ammonia would give 2,4-DNT, which can be recycled to the trinitration step; this concept was discussed above as an indirect approach to desulfonation. The hydrazino and dimethylamino derivatives were, however, obtained as fairly pure products, without isomer contamination, which suggests their possible use as chemical intermediates. The use of isomer mixtures should not be objectionable in biocidal applications. Arrangements have been made for biocidal screening of some of the amino derivatives, in view of the recent interest in dinitroaniline derivatives as weed killers (Ref 30).

Miscellaneous Reactions

With Ammonium Sulfide

A very low yield of 5,5-bis(2,4-dinitrotolyl) disulfide was obtained from 2,4-DNT-5-SO_3NA and ammonium sulfide (Ref 762-352-86).

Hydrolysis to 5-Hydroxy-2,4-DNT - Hydrolysis of the sulfonic acids to the cresols is potentially an interesting approach for recovery of the organic values, as follows:



(12)

The literature reports that this type of reaction is known for 2,4-DNB-SO_3Na. This report was checked as part of the present study using six different bases. The bases used and the yields obtained were as follows: MgO (0%); $NaHCO_3$ (22%); Na_2CO_3 (28%); NaOH (61%); CaO (83%); $Ba(OH)_2$ (84%) (Ref 762-387-68 to 70). With these results as a background, the similar hydrolysis of 2,4-DNT-5-SO_3Na was attempted using NaOH and $Ba(OH)_2$. Surprisingly, none of the desired product was formed (Ref 762-352-62,66).

Isolation of DNT Sulfonates from Red Water - Experiments were run at PA to see whether the sulfonates could be extracted in reasonably pure form. Evaporation of several samples of the red water to dryness gave an average recovery of 20.4% solids. Extraction of two solid samples with boiling dimethyl formamide gave 7.3% insoluble inorganics, based on the red water. These figures agree with those obtained at NSWC as cited above. Distillation of the solvent gave a mixture of the sulfonates and the red tar.

2,4-DNT-5-SO_3Na is ordinarily recrystallized from 90% isopropanol. A sample of pure sulfonate was found to give a 2.5% solution at the boiling point. On standing overnight at room temperature, 70% of the sulfonate separated and could be filtered. The filtrate comprised a 0.75% solution. The sulfonate was found to be too soluble in 80% isopropanol, and too insoluble in 100% isopropanol for satisfactory recrystallization (Ref 762-316-18,92).

The 3-SO_3Na on the other hand, was found to give at least a 13.5% solution in 90% isopropanol at the boiling point, and a 2:1 mixture of 5- and 3-SO_3Na formed at least a 7.5% solution at reflux. Thus, the mixture of sulfonates is, as expected, more soluble than the pure 5-isomer (Ref 762-387-38).

The mixture of sulfonates and red tar obtained using DMF was refluxed with 32.5 weights of 90% isopropanol, with the following results, based on the original sample of red water:

Isoluble:	1.4%
Separated on standing overnight:	4.2(A)
Soluble on standing overnight:	8.1(B)

The yield and low solubility in the cold solvent mixture of fraction A suggested that it might be fairly pure sulfonate, however, elemental and NMR analyses were inconclusive. Fraction B, on the other hand, appeared to contain sulfonates. Its IR spectrum closely resembled that of a 50-50 mixture of pure 3- and 5-SO_3Na, and NMR analysis also indicated the presence of the two sulfonates in equal amounts. However, the yield is about 60% higher than the total sulfonate content indicated by the NSWC analysis. Also, the elemental analysis of fraction B showed poor agreement with the theoretical for the pure sulfonates.

Direct extraction with boiling 90% isopropanol of the total solids obtained by evaporating the red water was next attempted. A 6.9% yield (based on red water) was obtained. This material generally resembled fraction B, in that it did not crystallize from the cold solvent, and was obtained only upon distilling the solvent off. This material was estimated to contain about 90% sulfonates based on thin layer chromatographic analysis run at NSWC.

Further evidence was obtained by nitric acid oxidation of the extracted solids (Ref 31). A blank experiment was first run in which pure 2,4-DNT-5-SO_3Na was refluxed for 6 hours at 118°C with 60% nitric acid. No fuming or other evidence of oxidation was noted, and the sulfonate was recovered unchanged in quantitative yield. A sample of material extracted from red water solids with 90% isopropanol was then treated similarly. A little fuming was noted. Workup gave an 80% yield of friable yellow solid found by NMR analysis to comprise 61% of 5-SO_3Na and 39% of 3-SO_3Na. This is in fair agreement with the 90% figure cited above, obtained at NSWC by thin layer chromatography. A third experiment was run similarly using the mixture of sulfonates and red tar as extracted from red water solids with DMF; only a sticky orange gum was obtained.

These experiments tentatively indicate that a mixture of 2,4-DNT-5- and -3-SO_3Na can be isolated in 80-90% purity from red water solids with boiling 90% isopropanol (Ref 762-316-81,91,92; 762-352-3).

It should be noted that the red tar fraction is apparently formed from 2,4,6-TNT as a result of unnecessarily drastic conditions during selliting as currently practiced. A study at Radford AAP (Ref 32) indicates that in part this involves selliting at unnecessarily high pH, resulting in the loss of about 70 lb. TNT/hr./line. In addition, the amount of sellite used is usually much more than necessary. A recent report (Ref 33) indicates actual usage in one case of 0.1 lb./lb. TNT, vs. an intended use of 0.063 lb. More rational selliting should at least greatly reduce red tar formation, and at the same time increase the yield of TNT, reduce sellite usage, and facilitate recovery of the sulfonates. Laboratory study of magnesium sulfite purification also indicates the absence of red tar formation (Ref 762-352-7).

Recovery of TNT Oxidation Products as TNB

It is known that several oxidation products of TNT are formed during nitration. These include TNBOH, TNBAL, and PiCOOH. Also present are TNB (resulting from decarboxylation of PiCOOH), and "white compound" (resulting from TNBOH or TNBAL under acid conditions). Since the alcohol, the aldehyde and the acid can easily be converted to TNB, an interesting explosive, it seemed of interest to consider their isolation from red water for this purpose. The rationale for this approach is discussed in detail in Appendix C.

An effort to recover these materials was made at RAAP (Ref 34). Red water was acidified, and the solid obtained was filtered. It was found to comprise almost entirely 2,4,6-TNT, containing a very small amount of TNB. The acidified solution was then extracted with methylene chloride, but evaporation of the solvent gave none of the oxidation products. No product was obtained upon extraction with ether. Simiiar results were noted in work at NSWC with Joliet red water (Ref 29). It was also noted at NSWC that TNB is decomposed by aqueous sodium sulfite (both buffered and unbuffered) at 85°C. It therefore seems unlikely that TNB, or its precursors, even if present, would survive the drastic conditions of selliting ordinarily used.

It was also found at NSWC that very little TNB or TNBAL is present in crude (unsellited) TNT, but they cite a RAAP report to the effect that the nitrobody from nitrator 6 contains 0.3% PiCOOH. The NSWC report accordingly recommends that the yellow water produced by washing crude TNT prior to selliting be analyzed for PiCOOH, and that, if an appreciable quantity is found, it be considered as a source for TNB.

The oxidation products should have appreciable solubility in the spent nitration acid, and it is suggested that it also be considered as a possible source, possibly by solvent extraction with methylene chloride with or without previous dilution.

PATENT STATUS

Patent proposals were submitted on various aspects of the above work, as follows:

a. Removal of TNM from TNT Plant Exhaust Gases (W.H. Gilligan and T.N. Hall, US Patent 4,003,977 (18 January 1977)).

b. Removal of TNM from TNT Plant Exhaust Gases (T.N. Hall and W.H. Gilligan, NSWC Case No. 58172, has been allowed and will issue early in 1977).

c. Recovery of 2,4-Diaminotoluene from TNT By-Products (E.E. Gilbert, 8 August 1973, PA Docket No. 4906).

d. Recovery of Toluidines from TNT By-Products (E.E. Gilbert, 8 August 1973, PA Docket No. 4907).

Applications were filed on both of the above disclosures; they were subsequently abandoned following the Patent Office contention that invention was lacking.

e. Recovery Process for TNT Purification Waste Water (E.E. Gilbert, 16 September 1976, PA Docket No. 5168).

This disclosure is concerned with the reaction of hydrazine with red water; a patent application was filed in mid-1977.

f. Recovery of 2-Amino-4-Nitrotoluene from TNT Purification Waste Water (E.E. Gilbert, 23 June 1977, PA Docket No. 5233).

CONCLUSIONS AND RECOMMENDATIONS

1. Methods have been developed for the recovery of TNM from TNT process exit gas. Further consideration should be given to scaleup of a TNM recovery process.

2. The best approach to the useful recovery of the 2,4-DNT-3- and -5-SO_3Na mixture in red water is desulfonation to 2,4-DNT, which could be recycled to the nitration step. No direct desulfonation method has been found; indirect procedures have been developed, but they are uneconomic. Further work on methods of direct desulfonation appears warranted, possibly including consideration of reductive approaches (e.g. electrochemical) and of photochemical desulfonation.

3. The reactivity of amino compounds with the DNT sulfonates is limited by steric and inductive factors. Primary aliphatic amines react easily with red water to give good yields of the mixed isomeric products. Hydrazine reacts easily with the 5-SO_3Na only. Ammonia gives lower yields of the isomer mixture. Efforts should be continued to find uses for the easily available amino derivatives.

4. A tentative method has been developed for isolation of the sodium sulfonate mixture from red water.

5. Conversion of the sulfonates to 2,4-DAT by reduction - desulfonation was shown to be feasible, but uneconomic in its present form because of high labor requirements. Further consideration toward reduction of the high labor cost appears warranted.

6. Location of the TNT methyl group oxidation products in the process should be established, and consideration given to their possible isolation as a practical approach to the preparation of TNB.

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Table 1

Reaction of ammonia, hydrazine and amines with pure 2,4-DNT-SO_3Na isomers

	3-SO_3Na					5-SO_3Na				
	Conditions[a]					Conditions[a]				
Compound reacted	Hrs.	°C	Percent yield	M.p. of product (°C)	Ref[b]	Hrs.	°C	Percent yield	M.p. of product (°C)	Ref[b]
Ammonia	1-2	95^d	30-36	93	36^c	1	95^d	40-85	193	27^c
Hydrazine	4-24	25-95	0-5	170	18	16	25	77	195	89^b
Methylamine	1.5	25	80	81	36	1.5	25	85	173	35
Dimethylamine	2.0	90	<5	Oil	80	1.5	25	82	110	80
n-Butylamine	0.5	90	84	Oil^f	37	0.5	90	90^+	96	26
Isopropylamine	0.5	90	35	95^f	27	0.5	90	75	69^f	27
Isobutylamine	0.5	90	67	53^f	49	0.5	90	92	96	28
n-Dodecylamine	0.5	90	90^+	Oil^f	86	0.5	95	83	61^f	66
Cyclohexylamine	0.5	90	86	Oil^f	79	0.5	95	86^g	133	77
Morpholine	-	-	-	-	-	1	95	14	152	32
Aniline	-	-	-	-	-	7	150^d	38-58	146	75^e

(a) All runs made with excess amine in dilute aqueous solution.
(b) Page in Notebook 762-387, except as indicated.
(c) Notebook 762-316.
(d) Run under pressure.
(e) Notebook 762-352.
(f) New compound.
(g) Yield 43% in 0.1 hr.

Table 2

Reaction of ammonia, hydrazine and amines with red water

	Gms. product per 100 ml. red water		Analysis[c]		Percent	
Compound reacted	25°[a]	95°[b]	5-	3-	yield[d]	Reference[e]
Ammonia	0 (24)	1.6[f,m]	72-8	22-8	23-46	27[g], 59
Hydrazine	2.2 (7)	1.5[f]	100	0	90+[i]	89[h],90[h],6
Methylamine	3.6 (1.5)	3.8[f]	57	43	90+	35,36,82,83,90
Dimethylamine	1.8 (1.5)	1.8[f]	100	0	75[i]	81
n-Butylamine	1.8 (5.5)	4.5	55	45	90+	26,37,91
Isopropylamine	0.8 (7)	3.4	57	43	81	27,48
Isobutylamine	1.4 (16)	4.4	52	48	90+	28,49
n-Dodecylamine	-	3.4	-[l]	-	90+[l]	66,86
Cyclohexylamine	1.8 (24)	5.6	57	43	90+	72[h],77,84
Morpholine	-	Very low[k]	-	-	-	32
Aniline	-	<1.5[j]	-	-	<38	75[h]

(a) Hours at 25° given parenthetically.
(b) All runs 0.5 hr., except as indicated.
(c) Of product prepared at 95°, by nmr, % given of designated alkylamino isomer.
(d) Crude yield of both isomers obtained at 95°, except as indicated, based on analysis at NSWC showing 2.5g. sulfonates (mol. wt. 284, 58% 5-(1.5g), 42% 3-(1.0g)) per 50 ml. (56g at s.g. 1.12).
(e) Page of Notebook 762-387, except as indicated.
(f) Run under pressure.
(g) Notebook 762-316.
(h) Notebook 762-352.
(i) Yield expressed on basis of content of 5-sulfonate.
(j) Run at 160° under pressure for 6 hrs.
(k) Heated for 1 hr.
(l) Analysis shows about equal amounts of the two isomers plus an impurity derived from dodecylamine.
(m) Three hr. reaction time.

APPENDIX A

PREPARATION OF PURE DNT SULFONATES

Preparation of 2,4-DNT-5-SO_3Na from 2,4,5-TNT

2,4,5-TNT (45.4 g - 0.2 m) and 100 ml water were heated with magnetic stirring to 60°C. A solution of anhydrous sodium sulfite (28 g - 0.22 m, 10% excess) in 125 ml water was added dropwise over 10 minutes, after which the solution was stirred for 30 minutes at 60-65°C. The solution was decanted from 0.5 g unreacted TNT, and cooled over night to crystallize the first crop of product, which was filtered. The filtrate was cooled in an ice bath and a second crop was obtained. The filtrate was taken to quarter volume, and cooled to yield a third crop. The crops were dried to constant weight, the weights being 29.0, 9.0 and 4.1 g, respectively; total 42.1 g (72%). Elemental analysis shows the product to be anhydrous. It is sufficiently pure for most purposes, but can be recrystallized from 90% isopropanol if desired. It is completely soluble in water (showing the absence of unreacted TNT) and in DMF (indicating the absence of inorganic salts). IR spectrum (KBr): 3580, 3460, 3100, 1630, 1520 (NO_2), 1440, 1360 (NO_2), 1225 (SO_3Na), 1050 (SO_3Na), 910, 830 (lone ring H), 710, 630, 590, 560, 420 cm^{-1}. Nmr (D_2O): δ 2.70 (S,3H,CH_3), 8.12 (S,1H,H_6), 8.48 (S,1H,H_3). (Ref Notebook 762-887-34 (Run 13)).

Notes: (1) Acidification of the dark red filtrate from the third crop with 10% HCl gave a solid (1.9 g) which decomposed explosively at 145°. (The structure of this compound is given in the section on Hydrolytic Desulfonation (Thermal)). Acidification of the filtrate from a run made at room temperature gave 5-hydroxy-2,4-DNT, rather than the diazo compound.

(2) A run similar to the above, but using equivalent sodium sulfite, gave 1.1 g unreacted TNT and a 92% yield of sulfonate (Ref 762-316-61 (Run 12)). Reaction at room temperature for 24 hours by the method of Brady et al. (Ref 4) gave a product containing both unreacted TNT and inorganic salts.

Preparation of 2,4-DNT-3-SO_3Na from 2,3,4-TNT

2,3,4-TNT (11.0 g - 0.049 m) and 20 ml water were heated with magnetic stirring to 65°, and a solution of anhydrous sodium sulfite (8.0 g - 0.064 m - 30% excess) in 40 ml water was added dropwise over 10 minutes, after which the solution was stirred for 30 minutes at 75-80°. The clear solution (there was no unreacted TNT) was held at 0° for an hour to induce crystallization; the solid was filtered and washed with a small quantity of ice water. The filtrate was evaporated to 30 ml, and again crystallized and filtered. The two crops were air dried to constant weight: 7.8 + 3.8 g = 11.6 g (75% of theory). Elemental analysis showed the product to be a 2.5 hydrate, in agreement with the literature (Ref 5). IR spectrum (KBr): 3500, 3100, 1620, 1530 (NO_2), 1360 (NO_2), 1250 (SO_3Na), 1180, 1130, 1050 (SO_3Na), 930, 850 (two adjacent aromatic protons), 760, 720, 615 cm^{-1}. Nmr (D_2O): δ 2.70 (S, 3H, CH_3), 8.12 (S, 1H, H_6), 8.48 (S, 1H, H_5). (Ref Notebook 762-316-102 (Run 7)).

Notes: (1) The above procedure is essentially that of Gornall and Robinson (Ref 5).

(2) Acidification of the filtrate from this preparation, unlike that cited above for the 5-sulfonate, did not give an explosive precipitate; much NO_x was evolved.

APPENDIX B

COST STUDY FOR RECOVERY OF DAT FROM RED WATER

Basis of Calculation: 1 DAT recovery unit servicing 3-60 T/D continuous TNT lines (180 T/D TNT production).

Operating cost summary •

Material	Cost per unit	Usage per day	Cost per day ($10)
Hydrogen*	$0.65 mscf	194 mscf	$126
NH_3	150/T	2.3T	345
$(NH_4)_2SO_4$**	56/T	8.9T	498
Labor***	3.75/man hr.	48 man hr.	180
Overhead	4.6 x labor		828
			1977
DAT credit$^+$	400/T	(3.78T)	(1512)
Net Operating Cost:			+465

• Per process on attached Flow Sheet

* Priced at $2.00 mm BTU = 0.65/mscf.

** Recycled by incineration with $SO_2 \rightarrow H_2SO_4$ recovery. Cost of recycle = $56/T (cf. Ammonium Sulfite Feasibility Study).

*** 2 men/shift = 48 m/d @ $3.75/man hr.

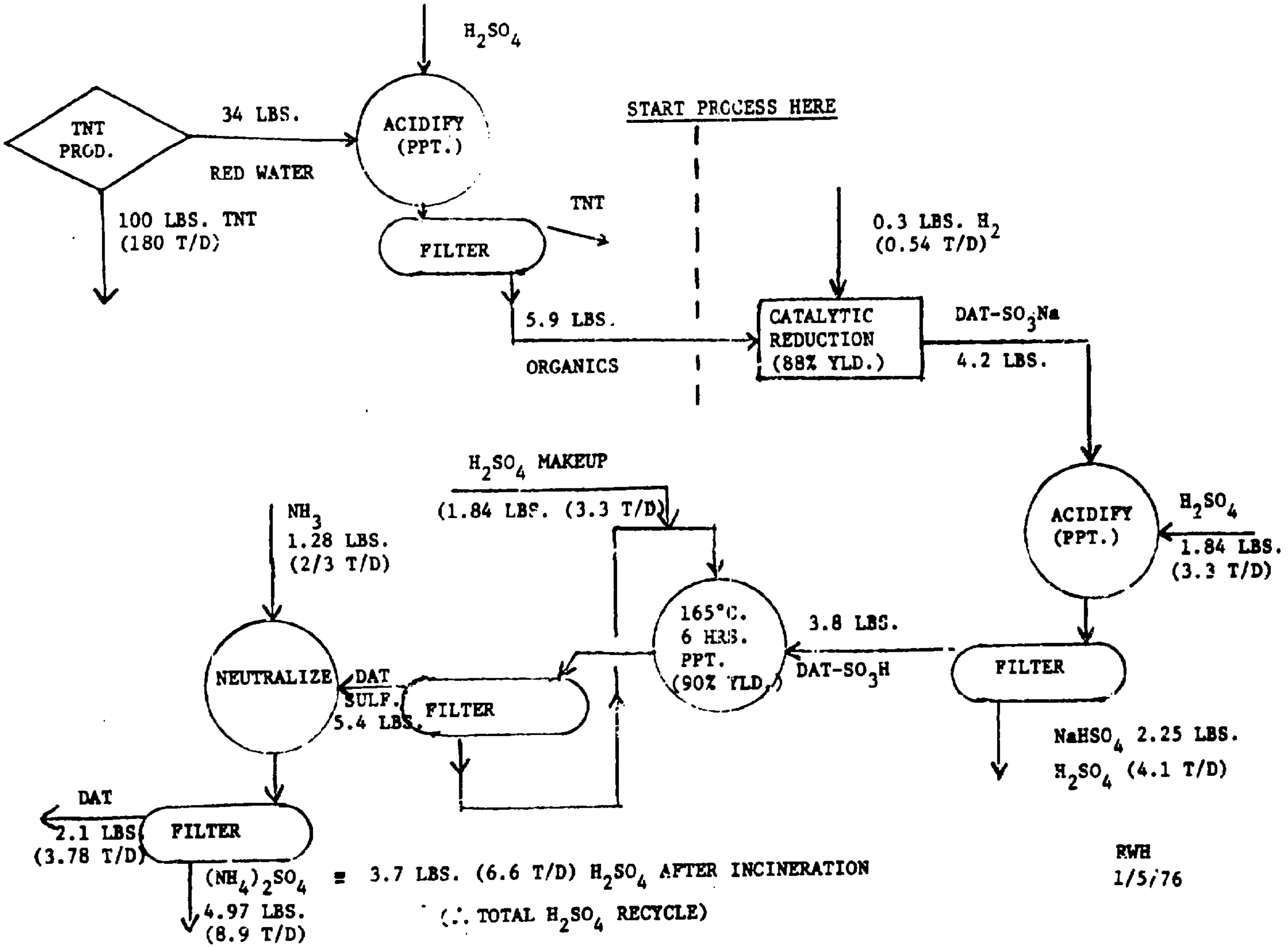
\+ 20¢/lb credit for DAT = $400/T.

Note: If equipment cost $1,000,000 (without H_2 production), then would add $1,000,000/10 yrs/365 D/yr = $274/D additional. (This is a guess; equipment could cost considerably more but hardly less).

Conclusion: Process not economically favorable.

R.W. Hutchinson
5 January 1976

RECOVERY OF DAT FROM RED WATER



RWH
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APPENDIX C

TNB RECOVERY FROM SPENT SELLITE SOLUTION

TNB has interesting and in some respects unique properties as an explosive, but its development has been blocked by the lack of a suitable process for its preparation. At present it is available only at fine chemical prices (ca. $130 per lb); and is made by chromic acid oxidation of TNT.

Recent studies at NOL have shown that TNB can be prepared in ca. 83% yields by the oxidation of TNT with nitric acid under pressure. This procedure is considered promising and will be studied further; production of TNB at 50¢/lb appears possible.

Dr. Kaplan of NOL has recently suggested that TNB be obtained from the by-product mixture obtained in preparing HNS from TNT. About 50% of the TNT is converted to this material, which comprises trinitrobenzaldehyde, trinitrobenzyl alcohol, trinitrobenzyl chloride and trinitrobenzene. Dr. Kaplan points out that it should be fairly easy to convert this mixture to TNB via trinitrobenzoic acid, possibly using nitric acid at reflux as the oxidizing agent. Experimental work to verify this approach is contemplated for FY74.

The purpose of this memorandum is to suggest consideration of another possible source for TNB, namely the spent sellite solution from TNT production. Recent analyses of spent sellite by Dr. W. T. Bolleter of Radford AAP shows that the major organic compounds present, aside from water soluble sulfonates, are as follows, expressed as pounds per 100 lbs TNT:

α-TNT sellite complex	1 2.3	
White compound salt	0.03 - 0.2	
TNB sellite complex	0.1 - 0.2	0.27 - 0.8
Trinitrobenzoic acid salt	0.03 - 0.2	
Trinitrobenzyl alcohol	0.07 - 0.2	
Trinitrobenzaldehyde sellite complex	0.07 - 0.2	

Acidification of the spent sellite with sulfuric acid would be expected to decompose the three sellite complexes to the parent compounds, which would precipitate being poorly soluble in the aqueous acid solution; the two salts would behave likewise. The solid mixture should be recoverable by filtration and/or solvent extraction. The aqueous filtrate should then be disposable by the same method as now used (utilization in paper manufacture), or by the reduction-hydrolysis approach suggested by the writer in a concurrent memorandum.

The solid mixture would then be refluxed with nitric acid, essentially as proposed by Kaplan. The aldehyde and alcohol should be thus converted to TNB via the acid. The oxidized mixture would then contain: 75% α-TNT; 20% TNB; 5% white compound. Crystallization should give α-TNT (recoverable for credit), TNB, and white compound (for discard). (Dr. Bolleter advises that proposed changes in the selliting operation will reduce the amount of α-TNT present, with the other compounds remaining the same. This would give a final oxidized mixture richer in TNB and in white compound than indicated above.)

The above approach would yield ca. 1-2 million pounds TNB per year assuming: (1) TNT production of 300 million pounds (2) all the spent sellite would be worked up as above.

E.E. Gilbert
27 March 1973

LIST OF SYMBOLS

2,4-DAT	2,4-Diaminotoluene
2,4-DAT-5-SO_3Na	2,4-Diaminotoluene-5-sulfonic acid, sodium salt
2,4-DNB-SO_3Na	2,4-Dinitrobenzenesulfonic acid, sodium salt
2,4-DNT	2,4-Dinitrotoluene
2,4-DNT-3-SO_3Na	2,4-Dinitrotoluene-3-sulfonic acid, sodium salt
2,4-DNT-5-SO_3Na	2,4-Dinitrotoluene-5-sulfonic acid, sodium salt
2,4-DNT sulfonates	A mixture of the above obtained from red water.
FEFO	Fluorodinitroethyl formal
NSWC	Naval Surface Weapons Center
PiCOOH	2,4,6-Trinitrobenzoic acid
RAAP	Radford Army Ammunition Plant
Red Water	Waste water from TNT purification
Sellite	Sodium sulfite solution used to purify TNT
3-SO_3Na	Same as 2,4-DNT-3-SO_3Na
5-SO_3Na	Same as 2,4-DNT-5-SO_3Na
TNB	1,3,5-Trinitrobenzene
TNBAL	2,4,6-Trinitrobenzaldehyde
TNBOH	2,4,6-Trinitrobenzyl alcohol
TNM	Tetranitromethane

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