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## THERMAL STABILITY OF ANFO MADE WITH RECYCLED OIL

By

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### ABSTRACT

The Pittsburgh Research Laboratory of NIOSH conducted research to determine the safe operating conditions for using recycled (used) lubricating oil from mining equipment as a partial replacement for diesel fuel to make ANFO-type blasting agents. The use of recycled oil (RO) conserves energy, reduces oil imports, and reduces mining costs.

Since RO has a variable composition, there was concern that the additives/impurities it contains may cause ANFO made with RO to be unstable (as compared to regular ANFO) at high summer ambient storage temperatures. Reactivity of RO with zinc was also a concern. Thermal stability tests were conducted to help quantify and resolve these issues. ANFO mixtures (0.66 lb/300 g) were put into sample containers made of steel, stainless steel, and galvanized (zinc coated) steel pipe fittings, which were heated in isothermal ovens. The experimental parameters were temperature settings of 140° F (60° C) and 176° F (80° C), four sample container (pipe fitting) metal combinations, and nominal heating periods of one and three days.

The ANFO samples contained 6% each of the following twelve different oils/oil mixtures: No. 1 was diesel fuel, Nos. 2 thru 6 were five candidate oils (2 thru 5 were used oils and 6 was a new synthetic oil), No. 7 was 5% diesel fuel + 1% graphite, and Nos. 8 thru 12 were 3% diesel fuel + 3% each of the five candidate oils. All samples showed no reactivity when heated at 140° F (60° C). All samples (except No. 7) reacted at 176° F (80° C) in a steel pipe with galvanized caps as follows: No. 1 reacted most, Nos. 8-12 reacted moderately, and Nos. 2-6 reacted least.

All ANFO samples were tested and found not to be cap sensitive.

## INTRODUCTION

The United States mining industry consumed about 5.4 billion pounds of ammonium nitrate-based industrial explosives in 1997.<sup>1</sup> Of these, about 4.2 billion pounds was ANFO and ANFO-type blasting agents. The usual ANFO formulation contains about 94% by weight ammonium nitrate (AN) and 6% diesel fuel oil (FO). If recycled (used) lubricating oil could be safely substituted for the fuel oil, up to about 36 million gallons could be consumed. This use of recycled oil (RO) can save energy and reduce oil imports. Consumption of used oil (generated by mines) on site, by blending it with diesel fuel to make ANFO-type blasting agents, could offer considerable cost savings to the industry.

The use of RO in ANFO may create blasting safety and performance problems, as well as health and environmental concerns. The blasting safety and performance concerns are especially significant at low ambient temperatures. These issues were addressed in our previous research paper.<sup>2</sup>

The focus of this current research at the Pittsburgh Research Laboratory (PRL) was to determine if RO could be safely used in ANFO blasting agents which were stored at high summer ambient temperatures in the southern United States. This experimental data on oil viscosity, ANFO cap sensitivity, and thermal stability is being presented to the mining industry and other interested parties. The worst-case concern is that once warmed in storage, the temperature of ANFO (made with RO) could rise further due to self-reactivity, and reach the point of ignition and subsequently detonation. Self-reactivity could arise due to contaminants which could catalyze an exothermic reaction. The contaminants could already be in the oil or AN, or be introduced during handling and storage (thru contact with metal surfaces etc.). One issue is the possible effects of zinc from galvanized steel. The PRL has previously published research on this hazard.<sup>3</sup> In that study when various mixtures of a AN, zinc, and compressor oil were heated rapidly (to 248° F or 120° C within 15 minutes), an exothermic reaction was observed at temperatures as low as 223° F (106° C). In our current research the samples were heated and held at lower temperatures for longer times.

Currently the permitted use of recycled oil in ANFO and heavy ANFO in the United States requires compliance with all applicable governmental agency regulations/requirements.<sup>2</sup> This includes the Mine Safety and Health Administration (MSHA) and the Environmental Protection Agency (EPA). For non-mining uses the Occupational Safety and Health Administration (OSHA) has jurisdiction. MSHA uses a Petition For Modification (PFM) process for its safety standard with respect to using RO in ANFO. This is because a previous safety publication on ANFO recommended that crankcase oil should not be used.<sup>4</sup> A PFM may be approved on a mine by mine basis, and is subject to certain limitations and testing. MSHA has discontinued the use of its Generic Petition, which was a guide to the PFM. However, some recent Petitions For Modification are currently available at the following Internet address: <http://www.msha.gov/readroom/petitions/menus/77.1304.htm>. Some of the provisions in these Petitions For Modification are specific to a particular mine, and are not applicable to other mines.

## EXPERIMENTAL WORK

### Specifications of Oils and Ammonium Nitrate Used

The ANFO samples tested contained 6% each of the twelve different oils/oil mixtures described as follows. They are also listed in table 1. The light colored oil samples were dyed dark red to help observe the mixing with AN prills.

To insure proper specification No. 2 diesel fuel (FO), a certified, analyzed batch (oil sample No. 1) was purchased directly from a refinery.

Two analyzed samples of RO (batches A and B), designated Nos. 2 and 3, were obtained from a mine approved by MSHA to use ANFO made from RO on site. These oils both met the EPA requirements for allowable levels of heavy metals (lead etc.), halogens (chlorinated solvents, and PCB's), and minimum flash point.<sup>2</sup> The oils are black in color, and a fine black residue settled out on standing. The residue is presumed to be a combination of carbon, graphite, and other insoluble materials. Because of this, all containers were well shaken before any sample was withdrawn. The particle size of this residue is controlled by a 100 mesh (147 micron) filter.

An SAE 10W-30 weight re-refined motor oil, made from recycled products and meeting American Petroleum Institute standards, was purchased from the U.S. Defense Supply Center (No. 4 - US).

An SAE 10W-30 weight re-refined motor oil, produced by a different manufacturer (No. 5 - AC), and a 10W-30 weight new fully synthetic motor oil (No. 6 - M) were purchased at a retail store. There was concern that synthetic oil might cause instability in ANFO.

Sample No. 7 was a mixture of five parts FO (No. 1) and one part graphite (Fisher Scientific Company \* #G67, grade #38). There was concern that graphite might cause instability in ANFO. Graphite has been used as an additive in motor oils, and/or it could be an oil contaminant (produced by pyrolysis reactions in an engine).

Numbers 8 thru 12 were 3% FO plus 3% each of samples 2 thru 6. ANFO was also made with 6% of oil samples 2 thru 5 which were 100% RO. This was done to maximize the level of additives/impurities of concern for test purposes. MSHA may restrict the percent of RO in ANFO on a mine by mine basis in petitions for modification of its safety standard. There are a number of other reasons why it may not be advisable to use more than 50% RO (3% of 6% oil) in ANFO in field blasting. Due to the possibly higher carbon content of RO, the oxygen to fuel balance of the ANFO may be shifted (if 6% oil is used). This could produce excessive levels of carbon monoxide. In addition, the concentrations of lead (and other heavy metals) in the blasting fumes would be increased. The ANFO may become cap sensitive due to increased levels of impurities from the RO, especially in hot conditions. Likewise, the water in RO may reduce sensitivity at some low temperatures (such as winter ambient conditions at northern mines).

Standard bulk blasting agent grade AN prills were purchased from a local explosive supplier. The bulk density is about 0.85 g/cc at room temperature. To maintain dry storage conditions, the prills were transferred to plastic buckets with two sealed inner plastic bags and lids.

## Viscosity Measurements

For comparison purposes the viscosities of the oils and oil mixtures, used to make the twelve different ANFO mixtures, are listed in Table 1. The viscosity measurements were made with a Brookfield \* model LVDV II + (rotary spindle) digital readout viscometer, with UL Adapter attachment. The temperature was controlled to within 0.1 ° C by an attached cooling jacket, connected to a bath circulating antifreeze solution. Each viscosity reading was checked at several different speeds. The values compared closely, indicating Newtonian behavior.<sup>5</sup>

## Cap Sensitivity

The blasting cap sensitivity of each of the twelve ANFO mixes listed in Table 1 was checked. All were found to be not cap sensitive (at 75° F = 24° C), and in all tests the lead witness cylinder showed no compression from its initial length.<sup>6</sup>

## Thermal Stability Measuring Equipment

In order to evaluate the thermal stability of the various ANFO mixes the following equipment was used. An ANFO sample holder was assembled from a threaded metal schedule 40 pipe nipple (2.5" x 6" = 6.4 cm x 15.3 cm) and two caps. The top pipe cap was drilled and tapped to accept a stainless steel compression fitting which held a stainless steel riser tube. This assembly had a minimum bore (venting diameter) of 0.296" (7.5 mm). The ANFO sample size was 0.66 lb (300 g), which loaded the pipe assembly slightly more than half full. The total sample height averaged about 4 1/4" (10.8 cm). This sample holder was placed in a laboratory oven (in a remote bunker), regulated by a digital temperature controller to ±1 °C. The riser tube projected out the top, through the oven vent hole.

A temperature probe, consisting of a 1/16" (1.6 mm) diameter stainless steel sheathed thermocouple, was inserted into the riser tube down to the middle of the ANFO. Another thermocouple was installed to record the oven temperature.

## Thermal Stability Measurement Method

The thermal stability was evaluated at 140° F (60° C). Additional tests were done at 176° F (80° C) to incorporate the United Nations Thermal Stability Test temperature of 167° F (75° C).<sup>7</sup> At the start of each test, the sample (in the pipe) and the oven were both at room temperature. Then the oven was turned on. The oven reached the test temperature after about one hour. The temperature probe (in the center of the ANFO sample) reached the oven set point temperature after about four hours.

Each ANFO sample was heated for one or three days minimum. Some samples run over the weekend were actually heated for almost five days (115 hours). Four different sample holder (pipe nipple + two caps) metal combinations were used: stainless steel nipple plus aluminum caps (considered to be non-reactive to AN), rusty steel pipe plus rusty iron caps, galvanized (zinc coated) pipe (which had some exposed rusty steel) and caps, and rusty steel nipples with galvanized caps. The ANFO was heated at 140° F (60° C) in the first three types of sample holders, and at 176° F (80° C) in the fourth. Galvanized fittings were used because they were a practical way to introduce the zinc into the test mixtures. Zinc can be a commonly introduced contaminant in the course of manufacturing, handling, and storing oils, AN, and ANFO. Zinc compounds are used as additives in lubricating oils. New (detergent-type) motor oil contains about 0.15% zinc.<sup>8</sup> There is a possible exposure to galvanized sheet metal and pipe fittings in tanks, bins, chutes, etc.

## THERMAL STABILITY RESULTS

Referring to table 1, mixes 1 thru 12 were heated in stainless steel/aluminum sample holders at 140° F (60°C) for one day (24 hours). No reactivity was observed. Mixes 1, 7, and 8 thru 12 were heated for at least three days (72 hours or more) at 140° F (60° C) in the following sample holder metal combinations: stainless steel/aluminum, steel/iron, and zinc/zinc. All were non-reactive (no self-heating was observed) on the basis of four indicators.

First, the temperature readout from the center sample thermocouple did not deviate significantly from the oven baseline temperature over the entire three-day heating period. At the end of the heating period the sample was examined. Second, there was no melting. Third, there was no color change. Fourth, the maximum measured weight loss (from 300 g of ANFO containing 18 g total oil) of any sample was only 1.10 g after 93 hours (almost four days). This weight loss was attributed to the evaporation of oil and water. The original AN prills, used to make the ANFO, could be expected to contain up to about 0.3% water. If any significant reactivity occurred, one would expect greater weight loss due to conversion of the oil and AN into evolved gaseous products such as N<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub>.

All 12 mixes were heated at 176° F (80° C) for three days or more in steel pipes with zinc caps. This metal combination was closer to actual field conditions, as compared to all steel/iron, or all zinc. A typical ANFO storage bin is mostly steel with some galvanized pipe fittings. Eleven of the 12 samples reacted to some extent with the zinc coating on the bottom galvanized pipe cap. See table 2 for details. Apparently the zinc acted as a fuel and was oxidized by the AN to form zinc oxide (a bulky white powder which is insoluble in water). There was also some carbonization of the oils which produced additional coloration, varying from light brown to black. The reaction product was in the form of a melted layer (1/32 to 1/4" or 0.8 to 6 mm thick, which ranged in coverage from about 5 to 100% of the bottom area) fused to the bottom pipe cap. In the reaction process, the zinc coating was partially to completely corroded to form the white zinc oxide. All the ANFO above the melted layer was unaffected, retaining its original color (red dye was added to the oil to judge the mixing with AN) and particle size except for caking. The center sample thermocouple (located about 1 3/4" or 4.5 cm above the layer) showed no temperature rise. The maximum measured weight loss (from 300 g of ANFO containing 18 g total oil) of any sample was only 1.04 g. To help determine the extent of reaction, the melted layer was scraped away to observe how much of the original zinc coating remained intact. This varied from zero to 100%.

A general pattern can be observed in the data in table 2, relative to the percent diesel fuel in the samples. Mix 1 with the most fuel oil (6%) was the most reactive. It was the only sample where part of the melt turned black. The melted layer was thickest (1/4" or 6 mm), and the zinc was completely burned away - which exposed all the iron underneath.

Mixes 8 thru 12 with 3% fuel oil plus 3% RO or motor oil were generally less reactive, with the melted layers varying from 3/16" or 5 mm to 1/32" or 0.8 mm thick. Mixes 2 thru 6 with 0% FO and 6% RO or motor oil were the least reactive, where the melted layers were all 1/32" or 0.8 mm thick. This pattern is understandable based on the chemistry involved.

Fuel oil is a good reducing agent. It contains easily oxidizable (combustible) unsaturated hydrocarbons which would react with AN (which is a good oxidizer) at elevated temperatures. In the manufacture of motor oil such hydrocarbons are purposely removed, because they would react with oxygen when heated causing the formation of sludge and carbon deposits harmful to an engine. Therefore, motor oil would generally be more resistant to combustion/oxidation/carbonization than fuel oil. Zinc is also a good fuel (reducing agent). The combination of 6% FO plus zinc tends to react (burn) with AN to a greater degree (at a given temperature) than 3% FO plus zinc, and 0% FO and zinc.

Another possibly significant factor, relative to the reaction of ANFO and zinc at 176° F (80° C), is that pure dry AN exhibits a crystal transition at 183.6° F (84.3° C), where heat is absorbed and the volume changes.<sup>9</sup> Due to moisture, clay coating, etc. this transition temperature could be shifted and occur closer to 176° F (80° C).

The chemistry involved in this overall process can also explain why, once a reaction started, the entire 300 g sample did not react at 176° F (80° C). The zinc oxide, once formed, can act as a chemical inhibitor of the decomposition of AN (to supply oxygen for combustion). In previous research publications zinc oxide was shown to inhibit the reaction of pyrite ore (a reactive fuel) with ANFO.<sup>10,11</sup> The zinc oxide can also act as a physical barrier between the ANFO and unreacted zinc. This appears to be the same mechanism that caused mix No. 7 (containing 1% graphite + 5% FO) to be non-reactive. The FO was totally absorbed into the prills, while the graphite formed an inert coating on the surface of the prills.

To determine if the higher temperature (176° F/80° C) would cause reactivity with the zinc absent, mixes 1 and 8 were heated in steel/iron for over six days (161 hours). There was no self-heating, no melting, no color change and the maximum weight loss was only 0.84 g.

## CONCLUSIONS

The ANFO mixtures tested at the PRL were non-reactive (under our specified experimental conditions) when heated in contact with steel, iron, and zinc at 140° F (60° C). Limited reactivity was observed at 176° F (80° C), but only when zinc was present. These results indicate (but do not guarantee) that other non-cap sensitive ANFO mixtures (made with properly selected and recycled oils) would probably be safe and stable under controlled field conditions. However, from a safety point of view, it must be noted that if any self-heating reaction occurs in a large quantity of ANFO (which is self-confining) the pressure and temperature can rise (faster than it can dissipate) to the point where the ANFO could burn and possibly detonate.

## RECOMMENDATIONS

ANFO mixes made with RO need to be evaluated for thermal stability before large scale field use, especially mixes intended to be stored under high ambient temperature conditions. The United Nations Thermal Stability Test Method <sup>7</sup> can be used to evaluate a small sample (50 g) by heating it in a covered glass beaker in an electric oven. The beaker should be placed in a metal tray, since the glass could crack when heated. This laboratory method could be modified (as required) to use larger samples or different containers, etc. Caution should be observed when an electric oven is used to heat a sample of ANFO to evaluate it for possible reactivity/thermal stability. Most electric ovens have interior parts that get hot enough to ignite oil vapors. If they build up to a high enough concentration, or if the ANFO “cooks off” there could be an explosion. Therefore, any such oven test should be conducted in a sufficiently isolated and secured building/room with adequate outside ventilation and with proper warning signs posted. In addition, the oven should be powered thru a timer or have a remote shut-off switch, to allow sufficient cooling time before personnel need to reenter the hazardous area.

Other appropriate larger scale field storage stability tests could be conducted in place of or in addition to the laboratory test.

The safe storage of ANFO made with RO is best assured by the following the applicable government agency recommendations and requirements.

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## APPENDIX

**Footnote:** \* Reference to specific brand names does not imply endorsement by NIOSH.

**TABLE 1 - COMPOSITION AND VISCOSITY OF OILS  
USED TO MAKE 94-6 ANFO MIXTURES**

OIL SAMPLE NO.	OIL(S) IN ANFO 6% TOTAL FUEL + 94% AN	VISCOSITY IN CENTIPOISE @ 70.0° F (21.1° C)
1	6% #2 Diesel Fuel Oil (FO)	2.6
2	6% Mine RO Batch A (RO-A)	118
3	6% Mine RO Batch B (RO-B)	156
4	6% US	163
5	6% AC	172
6	6% M	136
7	5% FO + 1% Graphite	6.4
8	3% FO + 3% No. 2 (RO-A)	11.7
9	3% FO + 3% No. 3 (RO-B)	12.6
10	3% FO + 3% No. 4 (US)	14.2
11	3% FO + 3% No. 5 (AC)	14.5
12	3% FO + 3% No. 6 (M)	13.7

**TABLE 2 - ANFO REACTIVITY AT 176° F (80° C), Observations Of Residues  
After Heating Samples For Three Days In Steel Pipes With Galvanized Caps**

MIX NO.	TEST NO.	COMPOSITION OIL(S) IN ANFO 6% TOTAL FUEL + 94% AN	SAMPLE COLOR	MELT			CONDITION OF ZINC AFTER MELT REMOVED
				COLOR*	THICKNESS, Inches (mm)	% OF CAP COVERED	
1	33	Regular ANFO (6% FO)	Red	Bk/Bn	1/4 (6)	100	All Removed
2	40	6% RO-A	Black	W/Bn	1/32 (0.8)	5	95% Intact
3	41	6% RO-B	Black	W/Bn	1/32 (0.8)	10	95% Intact
4	42	6% US	Red	W/R	1/32 (0.8)	70	95% Intact
5	43	6% AC	Red	W/Bn/R	1/32 (0.8)	25	95% Intact
6	44	6% M	Red	W/Bn/R	1/32 (0.8)	50	95% Intact
7	39	5% FO + 1% Graphite	Black	Did not melt			All Intact
8	34	3% FO + 3% No. 2 (RO-A)	Grey	W/Bn	1/16 (1.6)	100	80% Intact
9	35	3% FO + 3% No. 3 (RO-B)	Grey	W/Bn	1/32 (0.8)	30	95% Intact
10	36	3% FO + 3% No. 4 (US)	Red	W/Bn	3/16 (5)	100	80% Intact
11	37	3% FO + 3% No. 5 (AC)	Red	W/Bn	1/16 (1.6)	70	80% Intact
12	38	3% FO + 3% No. 6 (M)	Red	W/Bn	3/16 (5)	100	60% Intact

\* Bk = Black, Bn = Brown, R = Red, and W = White