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# BENÉT INTERNAL TECHNICAL REPORT

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**INVESTIGATION OF EXOTHERMIC GRINDING SLUDGE  
PRODUCED FROM WATERVLIET ARSENAL GUN STEELS,  
ANDERSOL WATER-BASED CUTTING FLUID, AND CINCINNATI  
MILACRON ALUMINUM OXIDE RESIN BOND GRINDING WHEELS**

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**Investigation Of Exothermic Grinding Sludge Produced From Watervliet Arsenal Gun Steels, Andersol Water-Based Cutting Fluid, And Cincinnati Milacron Aluminum Oxide Resin Bond Grinding Wheels**

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**Abstract**

The Advanced Technology Branch of Benét Laboratories, at the request of the Watervliet Arsenal Fire House, was tasked with the investigation of a Watervliet Arsenal exothermic grinding sludge. An on-site review of this grinding process showed that the grinding sludge apparently smoldered up to twenty-four hours after its production. In addition, within an hour, the sludge quickly reached a surface temperature that would cause a burn upon physical contact. At least one fire directly resulted from the inadvertent mixture of this sludge with a combustible material. Thermogravimetric analysis and x-ray fluorescence spectroscopy were used to chemically and physically characterize the grinding sludge. The data was compared with manufacturer information on the technical grade materials used in the grinding process. The thermogravimetric analysis data suggests the sludge was not smoldering but that it was evolving water in the form of steam as a result of the exothermic heating of the sludge from the oxidation of iron. This presents no immediate fire hazard unless the sludge is inadvertently exposed to combustible materials. It was recommended that an appropriate amount of inert sand or fire retardant powdered material should be well distributed throughout this exothermic grinding sludge as it is cooled and stored for disposal. It was further recommended that the grinding sludge should be stored safely away from combustible materials.

**Keywords**

Chemical/physical analyses, exothermic grinding sludge, Watervliet Arsenal gun steels, Andersol water-based cutting fluid, Cincinnati Milacron aluminum oxide resin bond grinding wheels, thermogravimetric analysis, x-ray fluorescence spectroscopy

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## Introduction

The Advanced Technology Branch of Benét Laboratories, at the request of the Watervliet Arsenal Fire House, was tasked with the investigation of a Watervliet Arsenal exothermic grinding sludge widely produced from Watervliet Arsenal gun steels, Andersol water-based cutting fluid, and Cincinnati Milacron aluminum oxide resin bond grinding wheels by a production grinding process.

An on-site review of this grinding process showed that the grinding sludge apparently smoldered up to twenty-four hours after its production. In addition, within an hour, the sludge quickly reached a surface temperature that would cause a burn upon physical contact. At least one fire directly resulted from the inadvertent mixture of this sludge with a combustible material.

Benét Laboratories was called upon to chemically and physically characterize the sludge, its chemical reactions, the degree of fire hazard, and possible recommendations for reducing the apparent fire hazard.

## Approach

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (1).

Technical grade materials from the Watervliet Arsenal include exothermic grinding sludge, gun steels, Andersol water-based cutting fluid, Andersol concentrate fluid, and Cincinnati Milacron aluminum oxide resin bond grinding wheels. Preparation of these materials involved only direct sampling.

Thermogravimetric data was acquired on a Perkin-Elmer Corp. Model TGA7. The sample weight ranges are 10 to 50 milligrams. The temperature ranges are 20° C to 850° C with a scanning rate of 20.0° C per minute.

Energy dispersive x-ray fluorescence spectrum was acquired on a Princeton Gamma Tech Corp. Model Four Plus with an International Scientific Instruments Corp. Model SR50A scanning electron microscope and its electron excitation source and vacuum sample chamber. The x-ray spectrometer has a silicon(lithium) liquid nitrogen cooled detector that provides a spectrum for the 0 to 20,000 eV energy range. The pulse processor or multichannel analyzer is an analog to digital converter whose signal is sent to a computer for analysis, processing, display, and communication. The analysis time per replicate is 100 seconds.

All sample data are analyzed in triplicate and are reproducible.

## Results and Discussion

The three components that compose the exothermic grinding sludge are Watervliet Arsenal gun steels, Andersol water-based cutting fluid, and Cincinnati Milacron aluminum oxide resin bond grinding wheels.

Table 1 gives the chemical specifications for Watervliet Arsenal 105, 120, and 155-mm gun steels (2). The major gun steel constituents that exceed one percent by weight are nickel, chromium, vanadium, and obviously iron.

Information on the composition of Andersol water-based cutting fluid is provided by its material safety data sheet (3).

This production cutting fluid contains twenty-four parts by volume water, one part by volume of Andersol concentrate, and has a pH of about eight. The main hazardous ingredient in the Andersol concentrate is sixty-one percent by volume chlorinated paraffin. The balance of the hazardous ingredients are mineral oil, nonylphenol ethoxylate, n-propoxypropanol, para-chloro-meta-cresol, and 2-amino-2 methyl-1-propanol.

The Andersol concentrate has a boiling point of 302° F (150° C) and has a flash point of 355° F (179° C). It is not pyrophoric, not an oxidizer, not explosive, and not reactive but it is flammable, combustible, and incompatible with strong oxidizers.

Figure 1 is a thermogravimetric analysis (TGA) of the Andersol concentrate. For the increase from room temperature to approximately 305° C, the weight loss is attributed to the more volatile components. For the increase from approximately 305° C to 435° C, the weight loss is attributed to the less volatile components. The data agrees well with the boiling point of Andersol concentrate and provides reasonable assurance that it meets the chemical specifications outlined in its material safety data sheet.

Figure 2 is a thermogravimetric analysis of deionized water. For the increase from room temperature to approximately 208° C, the weight loss is complete. The data agrees well with the boiling point of water.

Figure 3 is a thermogravimetric analysis of the Andersol production cutting fluid that is similar for used and unused solutions. For the increase from room temperature to approximately 175° C, the weight loss is attributed to most of the 96 percent by volume water present in the production cutting fluid. For the increase from approximately 175° C to 320° C, the weight loss is attributed to most of the 4 percent by volume Andersol concentrate present in the production cutting fluid. The data agrees well with the boiling points of water and Andersol concentrate and provides reasonable assurance that this production cutting fluid meets the chemical specifications outlined in its material safety data sheet.

Information on the composition of the Cincinnati Milacron aluminum oxide resin bond grinding wheel #97A46-K6-B80 is provided by the material safety data sheet and the product brochure (4,5). The 97A represents the aluminum oxide abrasive grit type with a titanium oxide impurity, 46 represents a coarse grit size, K represents a medium grade grit hardness due to moderate amounts of bond used, 6 represents a medium grit structure, and B80 represents a resinoid (plastic) type bond for the grit particles. This grinding wheel is 30 inches in diameter, 4 inches wide, with a 12-inch hole in the center, and a 1-inch recess on one side.

Figure 4 is an energy dispersive x-ray fluorescence (EDXRF) spectrum of this grinding wheel. The presence of aluminum (2339 counts at 1472 eV), titanium (178 counts at 4487 eV), and iron (305 counts at 6363 eV) is easily explained. The main chemical component of the grinding wheel is aluminum oxide with a titanium oxide trace impurity. The presence of iron is assumed to be from the gun steel that was imbedded in these used grinding wheels. The trace presence of calcium (146 counts at 3679 eV) is unexplained. This grinding wheel apparently has approximately 20 to 25 percent silicon (662 counts at 1731 eV) that is assumed to be from silicon carbide. The product information for this grinding wheel does not allow more than a trace presence (less than one percent) of silicon. This should be further investigated by the Watervliet Arsenal since no source of silicon is present in normal grinding wheel use.

The data agrees with the product information of this grinding wheel except for the silicon discussed above. Despite possible production concerns of this wheel's composition, it can be assumed that no additional fire hazards are added to the grinding operation because of these undisclosed variations.

Figure 5 is a thermogravimetric analysis of the grinding wheel. For the increase from room temperature to approximately 850° C, the weight loss is less than one percent and attributed mostly to the resin bonding material. The data agrees well with the chemical specifications outlined in its material safety data sheet.

Figure 6 is a thermogravimetric analysis of the grinding sludge. For the increase from room temperature to approximately 145° C, the weight loss is mainly attributed to water present in the production cutting fluid. For the increase from approximately 145° C to 275° C, the weight loss is mainly attributed to the Andersol concentrate present in the production cutting fluid. For the increase from approximately 275° C to 430° C, this constant weight region is attributed to the non-volatile steel particles and abrasive grit. The water and Andersol concentrate comprise approximately 55 percent of the grinding sludge, while the steel particles and abrasive grit comprise the remaining balance. The grinding wheel resin bond material comprises less than one percent of the grinding sludge. For the increase from approximately 430° C to 850° C, the weight gain is attributed to the oxidation of the iron or steel particles in the grinding sludge which shows that oxidation is possible. The data agrees well with the boiling points of water, Andersol concentrate, and grinding wheel resin bond material.

An energy dispersive x-ray fluorescence spectrum of the grinding sludge was not possible due to the problem of introducing an undried sample into the vacuum sample chamber.

Aluminum oxide or alumina abrasive grit ( $Al_2O_3$ ) does not present a fire or explosion hazard. It is practically insoluble in water or in non-polar organic solvents and is slowly soluble in aqueous solutions with the formation of hydroxides. It is also an adsorbent (6).

The oxidation of powdered iron or low alloy steel requires oxygen and water. The amount of metal surface area and the availability of oxygen and water at the metal surface determines the heat production per unit time of the reaction.

Oxidation is defined as combining with oxygen, dehydrogenating by the action of oxygen, changing a compound by increasing the proportion of the electronegative part, changing an element or ion from a lower to a higher positive valence, or removing one or more electrons from an atom, ion, or molecule (7).

For powdered iron or low alloy steel, electrochemical corrosion is a spontaneous reaction that may be pictured as a "short circuit" galvanic cell in which some regions of the metal surface act as cathodes and others as anodes. The electrical "circuit" is completed by electron flow through the iron or low alloy steel itself.

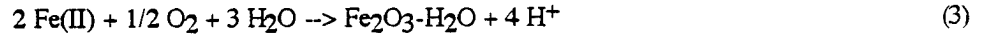
The anode reaction is:



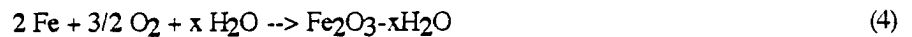
All ions exist in the aqueous state. Extensive corrosion takes place in contact with oxygen and water with the following cathode reaction:



For the secondary reaction, the Fe(II) ions can migrate to the cathode, where they are further oxidized by oxygen from air to the Fe(III) oxidation state to form Fe<sub>2</sub>O<sub>3</sub> ("rust") as a hydrated form of iron (III) oxide as follows:



The hydrogen ions produced in this reaction allow the corrosion cycle to continue. The overall reaction for the corrosion of iron is:



where x represents the number of moles of water available for this reaction (8,9).

Finely dispersed iron or low alloy steel powder oxidizes from readily to violently with moist air since it is a moderate reducing agent. As a result, if this powder is heated or ignited, it is moderately flammable or moderately explosive. Also, this powder is pyrophoric which means it spontaneously ignites. The oxidation products include Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> (6,10-13).

Powdered iron or low alloy steel can produce a moderate explosion if ignited in air due to the thermal expansion of atmospheric gases. The ease of ignition depends on the chemicals present, particle shape, particle size, particle surface, temperature, and ignition source.

One method of preventing ignition of this powder is to lower its exposure to oxygen or air by smothering the powder. Another method of preventing ignition or smoldering is to add and mix in inert powder. The well-distributed addition of an inert powder such as stone, sand, limestone, or fire retardant to an ignitable or smoldering powder may arrest the ignition (14).

The thermogravimetric analysis data suggests that the sludge is not smoldering as was thought but is evolving water as steam because of the exothermic heating of the sludge from the oxidation of iron. This presents no immediate fire hazard unless the sludge is inadvertently exposed to combustible materials. Considering this data, it is recommended that an appropriate amount of inert sand or fire retardant powdered material should be well distributed throughout this exothermic grinding sludge as it is cooled and stored for disposal. This action will reduce smoldering and possible ignition due to the exothermic nature of the various iron oxidation processes discussed. It is also recommended that the grinding sludge should be stored safely away from combustible materials and that it should be treated as any other exothermic source.

**Table 1. Chemical Specifications For Watervliet Arsenal Gun Steels**

<b>Element</b>	<b>Gun Steel Conc. Ranges</b>
Al	0.001 - 0.010
C	0.30 - 0.38
Cr	0.80 - 1.20
Fe	*
Mn	0.50 - 0.70
Mo	0.40 - 0.60
Ni	2.00 - 3.50
P	0.001 - 0.014
S	0.001 - 0.012
Si	0.15 - 0.30
Ti	0.001 - 0.015
V	0.08 - 0.12

\* Remainder Is Iron

# FIG. 1 - TGA OF ANDERSOL CONCENTRATE

TableCurve X-Y Data Table

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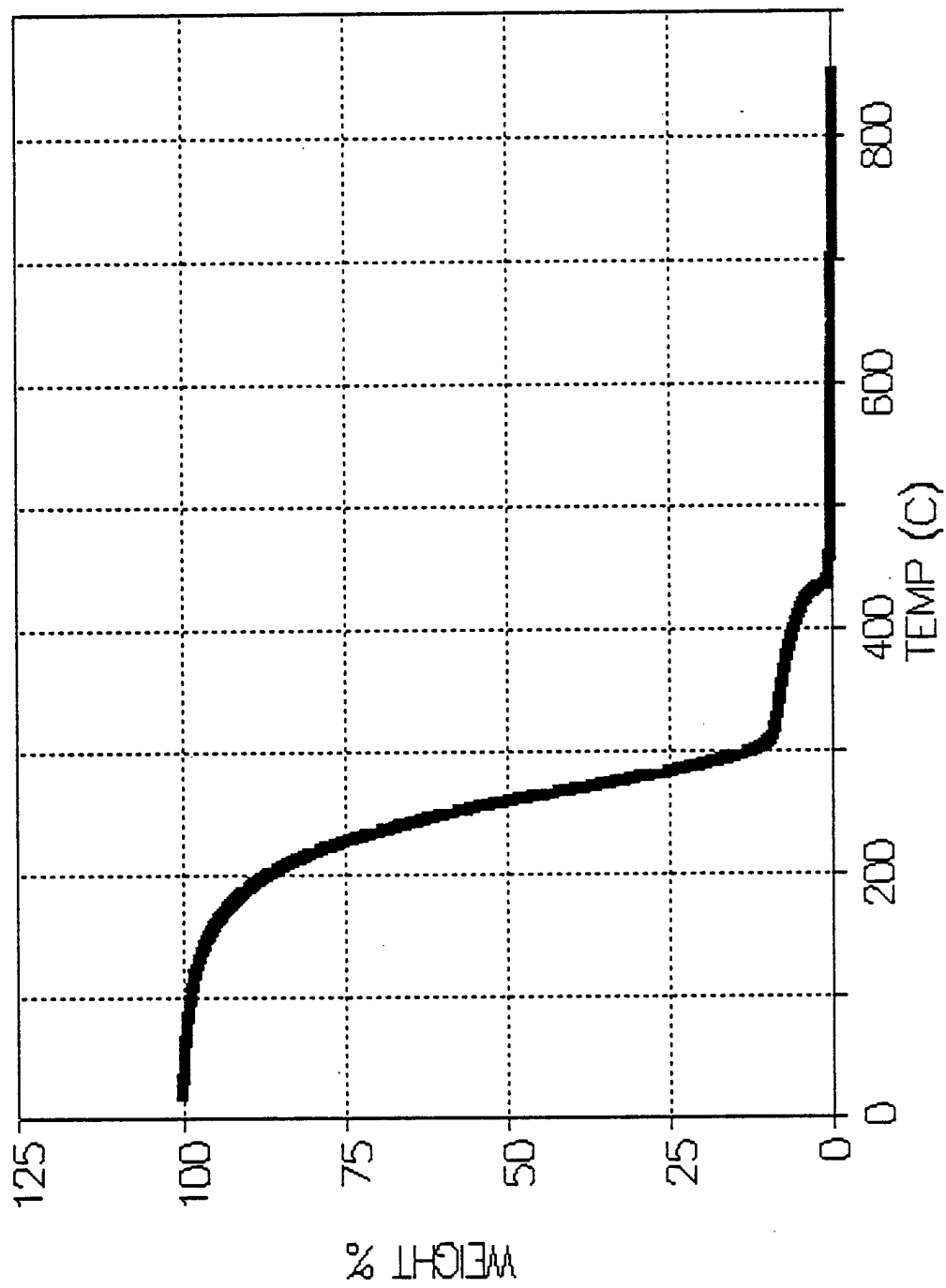


FIG. 2 - TGA OF WATER  
TableCurve X-Y Data Table  
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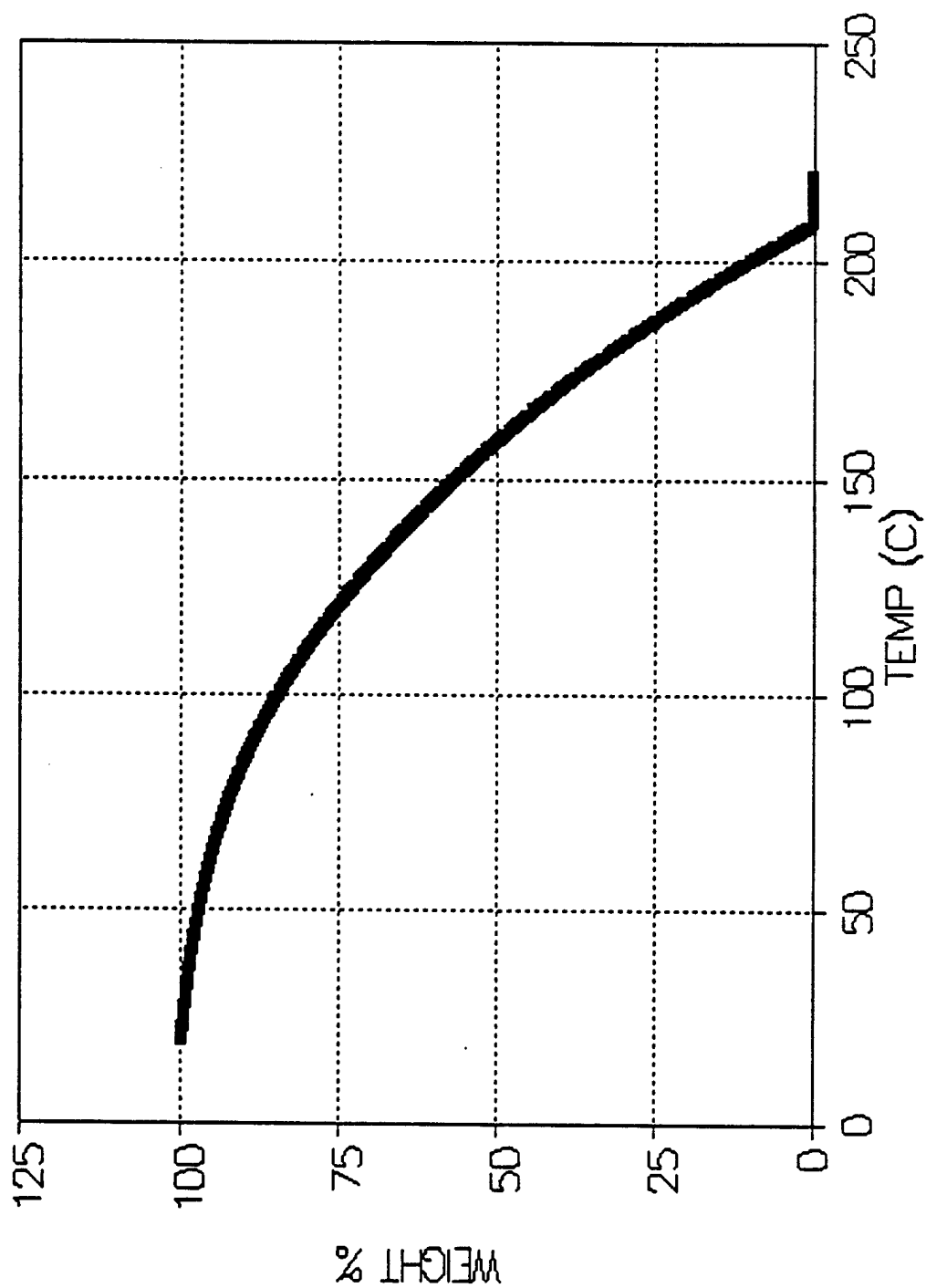


FIG. 3 - TGA OF ANDERSOL CUTTING FLUID

TableCurve X-Y Data Table

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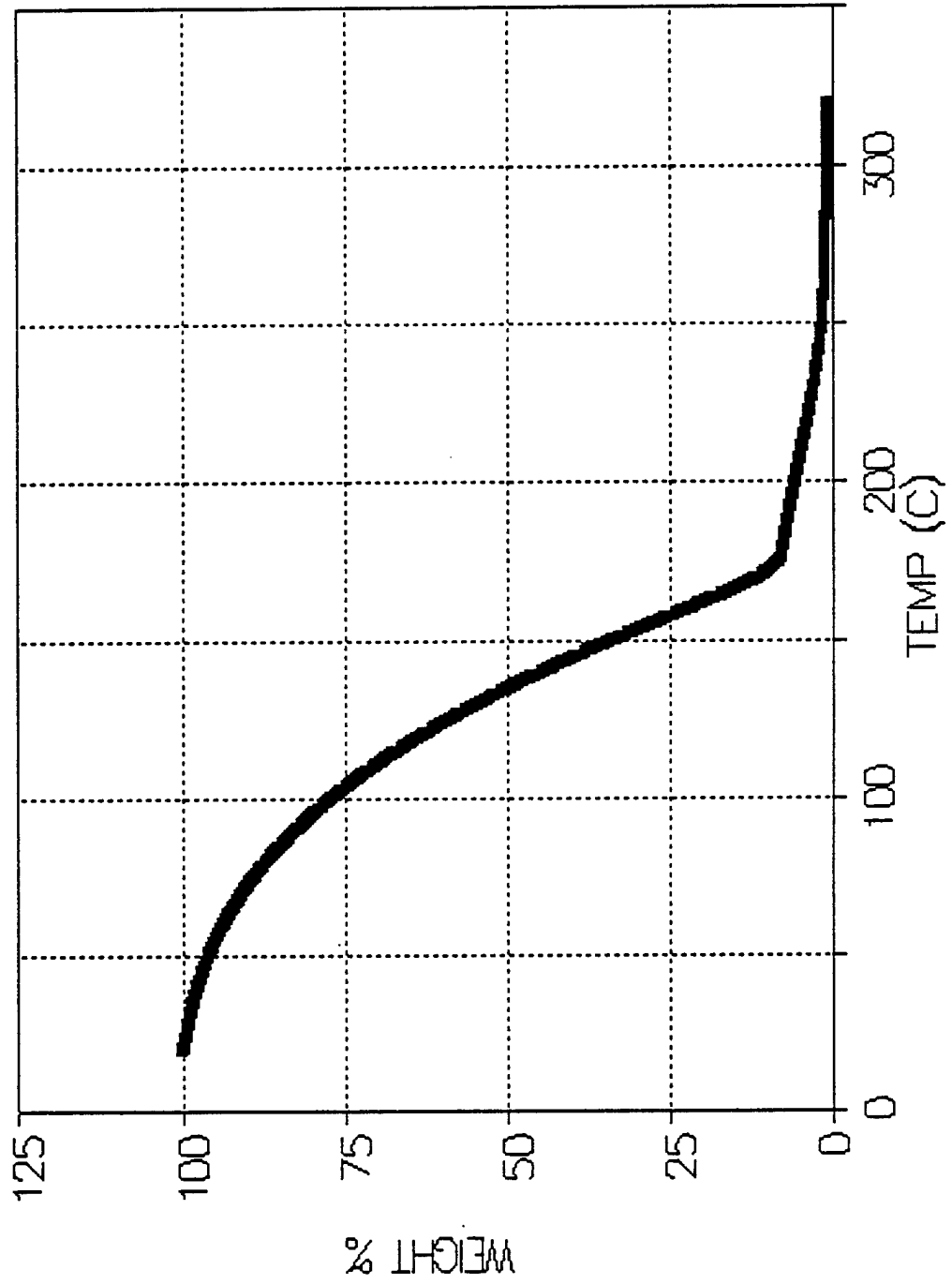


FIG 4 - EDXRF SPECTRUM OF GRINDING WHEEL

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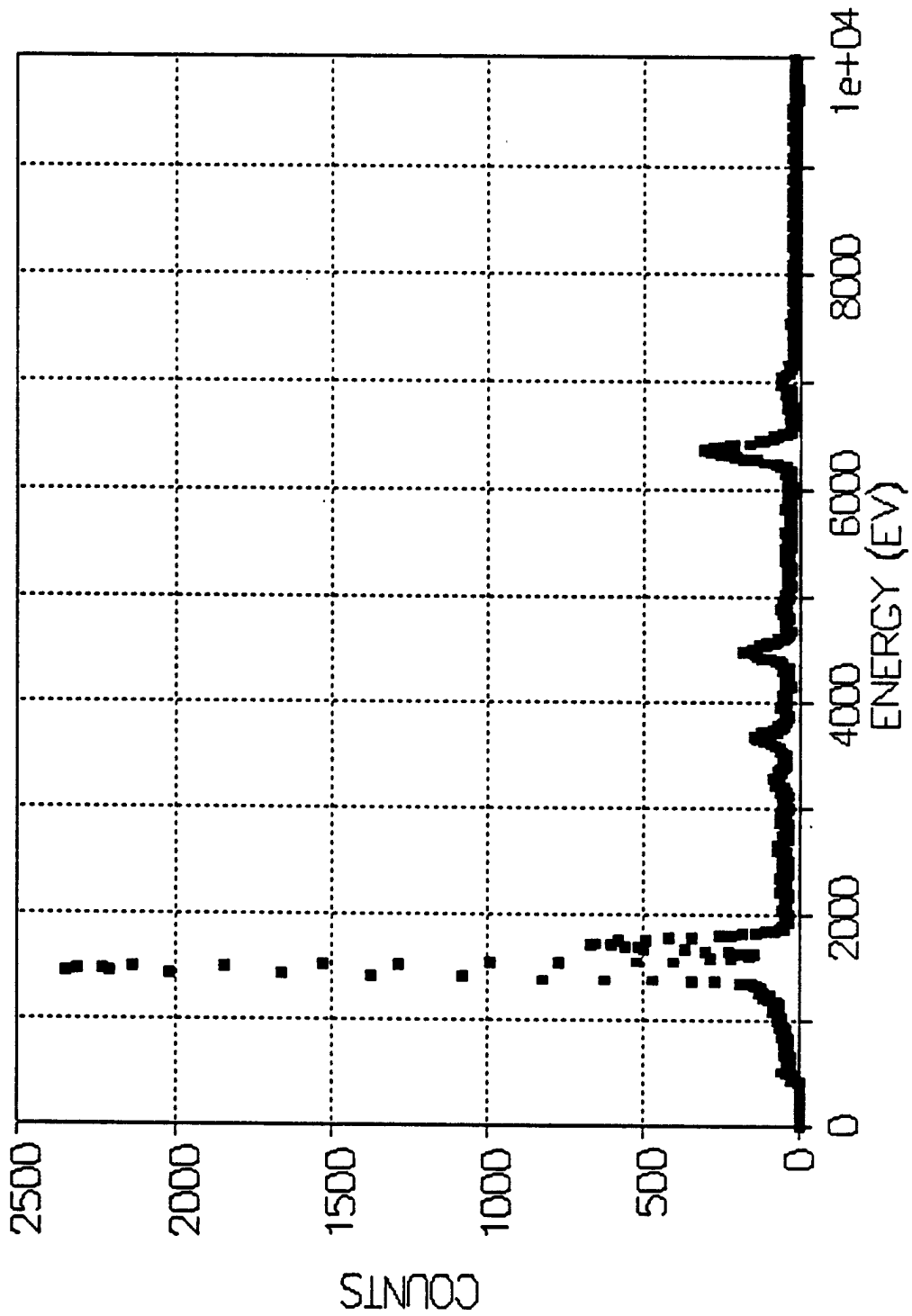


FIG. 5 - TGA OF GRINDING WHEEL

TableCurve X-Y Data Table

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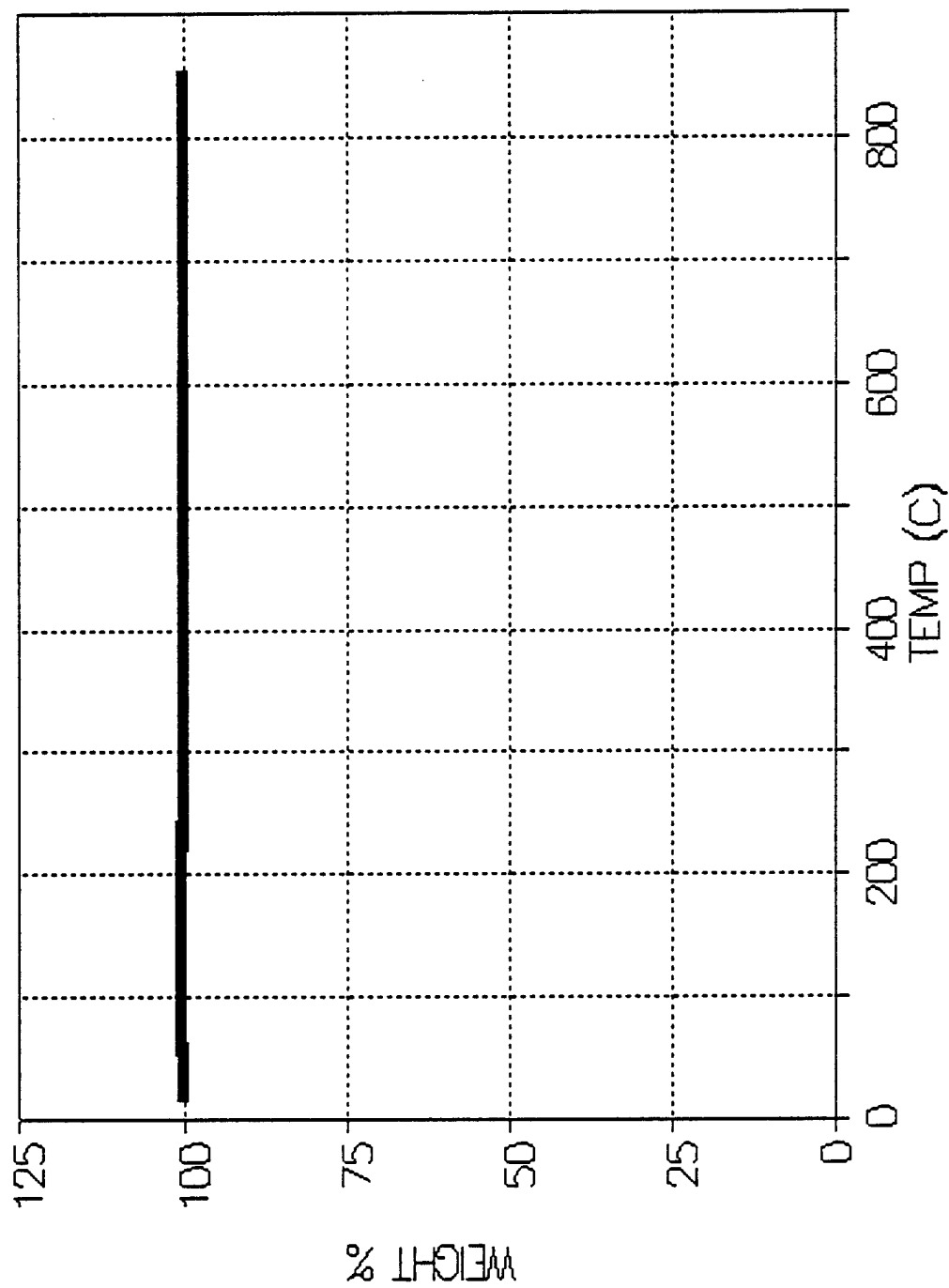
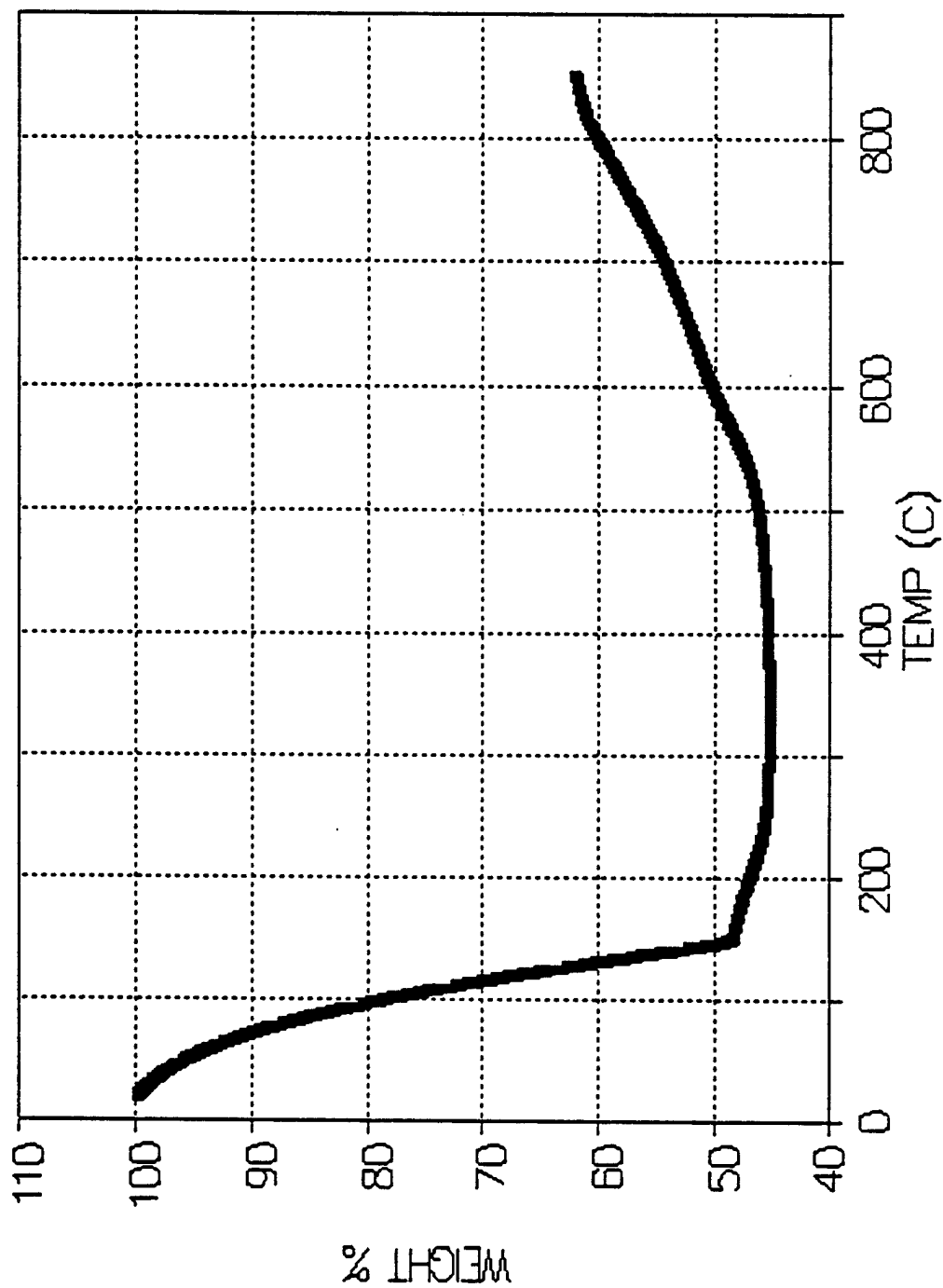


FIG. 6 - TGA OF GRINDING SLUDGE

TableCurve X-Y Data Table  
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