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FINAL SUMMARY REPORT

TO

AIR RESEARCH AND DEVELOPMENT COMMAND

ON

STUDIES ON STAINLESS STEEL AND ALUMINUM SLUDGES FROM NITRIC ACID CONTAINERS

Item II of

Contract No. AF 18(600)-53
E. O. No. 531-373HSR-8B
Project No. 53-630A-428

Task II of

Supplemental Agreement No. S2(53-453)

Southern Research Institute

Birmingham, Alabama

RESTRICTED
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BIRMINGHAM, ALABAMA

AUGUST 21, 1953

1748-235-XXXVIII

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ABSTRACT

Chemical, X-ray, and spectrographic analyses show that the insoluble corrosion product of aluminum in fuming nitric acid is $Al(NO_3)_3 \cdot 6H_2O$, and that the insoluble corrosion product of stainless steel containing columbium is a mixture of columbium carbide, silicon carbide, and anhydrous nickel nitrate. In another type of stainless silicon dioxide and anhydrous nickel nitrate are the insoluble products. The maximum solubility of the aluminum nitrate hexahydrate in ordinary white or red fuming nitric acids is about 0.1% at room temperature.

STUDIES ON STAINLESS STEEL AND ALUMINUM SLUDGES FROM NITRIC ACID CONTAINERS

I. INTRODUCTION

The original task set out in the contract was to "identify and analyze the sludge developing in fuming nitric acid after storage, to determine its particle size distribution, and to correlate its composition with changes in composition of the acid."

The corrosion products formed in metal containers during storage of nitric acid are of importance for several reasons. The formation of the sludge is the result of a chemical reaction between acid and container, a necessary consequence of which is a change in the composition of the acid. This change may be expected to influence the properties of the acid with respect to its ultimate use as an oxidiser for rocket propellants. A knowledge of the sludge should be an aid in evaluating container materials. These sludges create mechanical problems in handling and may contribute to erosive or abrasive wear in pumps and piping.

The two types of containers which have been used are stainless steel and aluminum. Work was begun on sludges from stainless steel drums but later developments indicated that aluminum might become a more important material, and, consequently, emphasis was shifted to aluminum sludges.

No particle size studies had been made on stainless steel sludges when work on them was discontinued with the concurrence of the Project Officer. Visual observations of changes in crystal size on standing and the small chance of being able to perform reproducible particle-size measurements on the samples available led to the decision not to attempt any experimental work along these lines with aluminum sludges. Some experiments attempting to produce aluminum sludges in the laboratory at an accelerated rate by treating 2S aluminum with fuming nitric acid at 75-80°C gave crystals of large and variable size. All these facts indicate that the history of the sample in terms of temperature cycling, rather than composition of acid, determines its particle size distribution.

II. STAINLESS STEEL SLUDGES

Several samples of sludges taken from stainless steel drums were studied with the purpose of learning their compositions. These samples were classified into two groups, one dark-colored and one light-colored. The analyses lead to the conclusion that the dark-colored sludges were derived from drums made from Type 347 steels and that the light-colored ones were derived from some other type of stainless.

Attempts to obtain X-ray diffraction patterns of these sludges while keeping the crystalline material in contact with the acid in order to avoid changes in composition by absorption of atmospheric water were not very successful and no positive identifications were obtained in this way.

The solid matter of these sludges was found to be 60-80% water-soluble. Analysis of the water-insoluble fractions of the dark-colored sludges by spectrographic and X-ray methods showed that the major components were columbium carbide and silicon carbide. The water-insoluble fractions of the light-colored sludges were found by chemical analysis to be about 85% SiO_2. X-ray diffraction patterns of this material were very diffuse and it was presumed that the silica was in an amorphous form.

Chemical analysis of the water-soluble fractions showed the following typical ratio of concentrations of metal ions for the dark-colored samples:

Ni, 48.6 parts
Fe, 3.0 "
Cr, 1.0 "

For the light-colored samples a typical ratio was:

Ni, 10.0 parts
Fe, 1.3 "
Cr, 1.0 "

From these data it was concluded that the major portion of the water-soluble solids was anhydrous nickel nitrate. This view is supported by reports in the literature that anhydrous nickel nitrate is formed when the hexahydrate is added to fuming nitric acid (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XV, page 487). The iron and chromium which accompany the nickel are there, in part, because the sample of water-soluble crystalline material was necessarily accompanied by an indeterminate amount of liquid-phase nitric acid. This liquid phase contained the metal ions in the following typical ratio:

Ni, 0.8% by weight
Fe, 2.7 "
Cr, 0.7 "

III. ALUMINUM SLUDGES

The identity of the colorless, crystalline sludge present in fuming nitric acid after storage in aluminum drums was suggested by a paper of Seligman and Williams (J. Chem. Soc., 109, 612 (1916)). Experimental evidence was given by them to show that crystalline $Al(NO_3)_3 \cdot 6H_2O$ is formed when aluminum is dissolved in nitric acid of specific gravity 1.5. In the presence of acid of specific gravity 1.42, the nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$, is the stable form.

In order to confirm this, several samples of sludge taken from aluminum drums (WADC samples) as well as some samples prepared in the laboratory (SRI samples) were analysed by the method of Seligman and Williams. The results are summarized in Table I. The calculated percentage Al_2O_3 for the hexahydrate is 15.87. For the nonahydrate it is 13.59.

Table I

Analysis of Aluminum Sludge

Sample	H_2O in Liquid Phase, %	Al_2O_3 in Sludge, %
SRI 1	7.6	15.9
SRI 2	5.4	15.1
WADC 8	6.0	16.1
WADC 12	2.2	15.5
WADC 14	6.7	15.7
WADC 23*	5.9	17.3

*Only 50 milligrams of sludge were available for analysis.

Although these results vary considerably, they confirm that the sludge is essentially $Al(NO_3)_3 \cdot 6H_2O$, and that this compound is stable when the H_2O concentration is as high as 7.6%.

The solubility at room temperature of aluminum nitrate hexahydrate in nitric acid of various H_2O and NO_2 concentrations has been investigated to a limited extent. Aluminum concentrations were determined by two independent methods with concurring results. In all cases the liquid and solid phases had been in contact at room temperature for at least several weeks when the liquid phase was analyzed. The results are shown in Table II. Samples A, B, and C were prepared at SRI. The others were received from WADC on 29 August, 1952. Solubility is expressed in terms of percent Al. Iron concentrations are given as a matter of incidental interest. The highest Al concentration occurred in the sample which was also highest in NO_2, but intermediate in H_2O. The lowest Al concentration occurred in the sample which was lowest in H_2O and also low in NO_2. Otherwise not much can be inferred about the effect of NO_2 or H_2O on the solubility of the salt. It appears that no more than about 0.06-0.10% Al will be found in ordinary white or red (6-7% NO_2) fuming nitric acid.

Table II

Solubility of Aluminum Nitrate Hexahydrate in Nitric Acid

Sample	% Fe	% NO_2	% H_2O	% Al
A	0.006	10	2.6	0.10
B	0.0003	1.1	0.4	0.014
C	0.0007	0.7	4.0	0.06
8	0.0007	9.0	1.9	0.06
17	0.002	8.7	4.2	0.05
19	0.013	6.4	5.3	0.04
21	0.006	5.4	4.1	0.05

IV. ACKNOWLEDGMENTS

Mrs. Ruby H. James performed the chemical analyses and Mr. Jack McLain did the spectrographic and X-ray diffraction analyses.

Submitted by
William J. Barrett

Locke White, Jr.

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