[CONTRIBUTION FROM THE BAROID DIVISION, NATIONAL LEAD COMPANY[1]]

# Preparation of Graphitic Oxide

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The preparation of graphitic oxide by methods described in the literature is time consuming and hazardous. A rapid, relatively safe method has been developed for preparing graphitic oxide from graphite in what is essentially an anhydrous mixture of sulfuric acid, sodium nitrate and potassium permanganate.

## Introduction

Graphitic oxide, sometimes called graphitic acid, has been known for almost a century. It was first prepared by Brodie[2] in 1859 by repeated treatment of Ceylon graphite with an oxidation mixture consisting of potassium chlorate and fuming nitric acid. Since then, many other procedures have been devised for forming graphitic oxide, nearly all dependent upon strong oxidizing mixtures containing one or more concentrated acids and oxidizing materials.[3-6]

The methods most commonly used at the present time are the original Brodie synthesis and one described by Staudenmaier,[6] in which the graphite is oxidized in concentrated sulfuric and nitric acids with potassium chlorate. Recent workers in the field such as Hofmann and Frenzel[5] and Hamdi[7] using the Staudenmaier method found the process time consuming and hazardous. The Staudenmaier–Hofmann–Hamdi method involved the addition of potassium chlorate to a mixture of concentrated sulfuric acid, concentrated (63%) nitric acid and graphite. The potassium chlorate was stirred slowly and carefully into the mixture over a period of one week with cooling. The chlorine dioxide evolved was removed with an inert gas such as carbon dioxide or nitrogen. The process required more than 10 g. of potassium chlorate for each gram of treated graphite and explosion was a constant hazard.

In the present method,[8] the oxidation of graphite to graphitic oxide is accomplished by treating graphite with essentially a water-free mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate. The entire process requires less than two hours for completion at temperatures below 45° and can be carried out safely providing reasonable care is maintained in observing the temperature limitations.

## Experimental

The graphitic oxide was prepared by stirring 100 g. of powdered flake graphite (Dixon's #635, 325 mesh) and 50 g. of sodium nitrate into 2.3 liters of 66° Be technical sulfuric acid. The ingredients were mixed in a 15-liter battery jar that had been cooled to 0° in an ice-bath as a safety measure. While maintaining vigorous agitation, 300 g. of potassium permanganate was added to the suspension. The rate of addition was controlled carefully to prevent the temperature of the suspension from exceeding 20°.

The ice-bath was then removed and the temperature of the suspension brought to 35 ± 3°, where it was maintained for 30 minutes. As the reaction progressed, the mixture gradually thickened with a diminishing in effervescence. At the end of 20 minutes, the mixture became pasty with evolution of only a small amount of gas. The paste was brownish grey in color.

At the end of 30 minutes, 4.6 liters of water was slowly stirred into the paste, causing violent effervescence and an increase in temperature to 98°. The diluted suspension, now brown in color, was maintained at this temperature for 15 minutes. The suspension was then further diluted to approximately 14 liters with warm water and treated with 3% hydrogen peroxide to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. Upon treatment with the peroxide, the suspension turned bright yellow. The suspension was filtered resulting in a yellow-brown filter cake. The filtering was conducted while the suspension was still warm to avoid precipitation of the slightly soluble salt of mellitic acid[9] formed as a side reaction.

After washing the yellowish-brown filter cake three times with a total of 14 liters of warm water, the graphitic oxide residue was dispersed in 32 liters of water to approximately 0.5% solids. The remaining salt impurities were removed by treating with resinous anion and cation exchangers. The dry form of graphitic oxide was obtained by centrifugation followed by dehydration at 40° over phosphorus pentoxide *in vacuo*.

## Results

The effectiveness of the oxidation method can be judged by the proportion of graphitic oxide in the product or by its carbon to oxygen ratio. Well reacted samples of graphitic oxide will have a carbon to oxygen atomic ratio lying between 2.1 and 2.9. Also the color of the product when suspended in water may be used as criterion for the degree of oxidation of the graphite. The product richest in graphitic oxide will have a bright yellow color whereas poorer samples with higher carbon-to-oxygen ratios will have a green to black hue.

An analysis of the dried graphitic oxide prepared by the present method is compared in Table I with a sample made by the Staudenmaier procedure. The present synthesis resulted in approximately 188 g. of graphitic oxide containing 23% water and 2% ash. The carbon and hydrogen were determined by the combustion of graphitic oxide with cupric oxide.[10,11]

TABLE I

| | % by weight | | | | Carbon-to-oxygen atomic |
|---|---|---|---|---|---|
| Method | Carbon | Oxygen | Water | Ash | ratio |
| Acid–permanganate–nitrate | 47.06 | 27.97 | 22.99 | 1.98 | 2.25 |
| Staudenmaier | 52.11 | 23.99 | 22.22 | 1.90 | 2.89 |

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