SUMMARY

1. The study of the reactions of sodium benzylate with aromatic nitro compounds as oxidizing agents has been extended to include o-, m-, p-nitrotoluene, o-, m-, p-nitroanisole, o-, m-, p-nitrophenetole and m-dinitrobenzene.

2. Optimum conditions have been found for obtaining the maximum percentage yields of benzoic acid and of the respective azoxy-, azo-, or nitrohydrazocompounds.

3. The preparation and properties of the new compound, 3-3[1]-dinitrohydrazobenzene, are reported.

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# DETERMINATION OF THE DEGREE OF HYDRATION OF MAGNESIA IN DOLOMITIC LIMES

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Hydrated limes made from dolomites quarried at Woodville and Gibsonburg, Ohio, are plastic, and hydrated limes made from dolomites quarried at all other places are not plastic. No reason for this unusual and valuable property of the Ohio dolomites has ever been discovered. All experiments and experiences indicate that this property depends in some way upon the magnesia.

At the plastic lime plants in Ohio the greatest care is taken to burn the lime at the lowest possible temperature. Too high a temperature is known to prevent the plastic property. No other single factor in manufacturing seems important inasmuch as all the other factors or conditions such as type and size of kiln, kind of fuel, type of hydrator, quantity of water used in hydration, and type of mill for final grinding are different in the different plants. On the other hand, no one has been able to burn any rock other than from this Ohio district into a plastic finishing hydrate in the ordinary commercial kilns. The scientific reason for this unusual quality of the Ohio finishing limes is interesting both in theory and in practice.

The low temperature of burning of these Ohio limes without doubt produces active magnesia. Campbell[2] showed that magnesia made by burning magnesium carbonate at 1000° C. hydrated to the extent of 18 per cent in one day, but if it was made at a temperature of 1100° the hydration dropped to 7 per cent, and if burned at 1200° the hydration was only 0.43 per cent. Johnston[3] found that magnesite decomposed at 756° and calcium carbonate rock at 898°. Artificially made magnesium carbonate decomposed at a lower temperature. A natural dolomite de-

[1] A portion of the thesis submitted by Mr. Fox for the Ph.D. degree at Indiana University in 1927. Delay in publication was due to the death of Mr. Fox.

[2] Jour. Ind. Eng. Chem., 1:665 (1909).

[3] J. Amer. Chem. Soc., 32:938 (1910).

composed at a lower temperature. A natural dolomite decomposed at about 835°, which indicated that the dolomite tested was a compound of magnesium and calcium carbonate and not a mixture of the two. In commercial burning of the dolomitic lime the temperature must be high enough to decompose the calcium carbonate also.

High temperature, besides affecting the magnesia, causes chemical combinations between the magnesium, calcium and iron oxides and the silica and alumina forming silicates and aluminates. The effect of this reaction may be very important, although it has not been considered by anyone as having an effect on plasticity.

A determination of the quantity of water with which the magnesium oxide combines or with which it can be made to combine is an accurate measure of the activity of the magnesia. Richardson's[4] thermal method of determining the hydrated magnesia in the hydrated lime is based upon the fact that magnesium hydroxide loses its water and becomes anhydrous at a much lower temperature than does calcium hydroxide or other constituents in the lime. He judged the temperature of decomposition of the magnesium hydroxide from breaks in "temperature loss in weight" curves made by plotting the weights of the samples heated for twenty-minute periods at regularly increased temperatures. His conclusion from ten different hydrated limes was that there was no relation between the per cent of magnesium hydroxide and the quality or commercial value of the lime. For example, two non-plastic hydrates showed 19.5 and 13.9 per cent of their magnesia present as the hydroxide, while a plastic hydrate from Woodville showed 10.7 per cent. It is possible that the age of the samples may have given the magnesia a chance to hydrate during storage. All freshly manufactured hydrates in the table did show lower degrees of hydration.

The object of this research was to determine the quantity of unhydrated magnesium oxide in the hydrated lime which would hydrate or react with water if soaked with water over night. This soaking over night is necessary commercially to develop the plasticity of the plastic Ohio hydrated limes. It was thought that the special properties of the plastic limes might be due not to the quantity of magnesium hydroxide in the original dry hydrated lime as determined by the method of Richardson but to the additional magnesium hydroxide which formed during the usual soaking preparatory to its use. Richardson showed in one sample that soaking increased magnesium hydroxide from 7.2 per cent to 11.9 per cent.

## METHOD OF ANALYSIS

The samples of hydrated limes were weighed into porcelain boats which were placed inside large Pyrex tubes containing pans of calcium oxide. These tubes were then heated in an electric furnace. The purpose of the calcium oxide was to absorb carbon dioxide from any air which might leak into the tube and to absorb the water evolved by the sample when heated. This procedure was easier than that of Richardson in which a very rapid current of pure air was passed over the

[4] Jour. Amer. Chem. Soc., 19:625 (1927).

samples in the tubes. The samples were first dried at 105° to remove simple extraneous moisture. Then they were dried at 360° to determine the water already combined with magnesium oxide from which the hydrated magnesia in the limes was calculated. The samples were then moistened with distilled water and, after twelve hours, were dried at 105° to a constant weight. They were then heated at 360° to a constant weight. The difference between these two weights gave the total hydrated magnesia. Subtraction of the hydrated magnesia originally present from this total value gave the hydrated magnesia which was formed by the soaking. The plasticity numbers are given in the table and the limes are arranged in the order of decreasing plasticities.

| Plasticity | Per cent magnesia already hydrated | Per cent magnesia hydrated during soaking |
|---|---|---|
| 296 | 14.3 | 16.5 |
| 180 | 6.9 | 9.1 |
| 172 | 8.1 | 14.1 |
| 166 | 8.6 | 6.6 |
| 150 | 11.1 | 16.6 |
| 147 | 4.6 | 18.1 |
| 128 | 2.7 | 14.7 |
| 106 | 2.8 | 10.8 |
| 55 | 4.8 | 11. |

Numerous experiments upon limes burned in the laboratory at various temperatures and under varying conditions showed that the magnesia hydrated to a greater extent the lower the temperature and the shorter the time of heating. A survey of all the results shows no regularity between plasticity and the magnesium hydroxide present either in the original lime or formed during soaking.

## POSSIBLE SOURCES OF ERROR

A. The soaked samples were dried at 105° for weighing, whereas in regular commercial work hydrated limes are soaked without any heating. It may have been that the heating during drying caused the magnesia in the non-plastic hydrates to react with water about as completely as did the plastic limes. No way could be devised to avoid this possible error.

B. It may be that silicates and aluminates as well as magnesia react with water and lose water when dried at 360°. However, only small quantities of such compounds are possible because most limes tested contained less than one per cent of such impurities.