

## NOTES ON THE PRECIPITATION OF MAGNESIUM HYDROXIDE.\*

BY ROBERT WOOD TERRY AND EDWARD D. DAVY.

These notes are a partial study of the chemistry of the precipitation of magnesium hydroxide with particular reference to the manufacture of "milk of magnesia" by the precipitation process, using magnesium sulphate and sodium hydroxide as the basic materials.

Each experimental lot consisted of quantities sufficient to make 100 mls of finished magma and both the magnesium sulphate and sodium hydroxide solutions were diluted to 400 mls and mixed in the manner noted in the tables; this is the same concentration directed by the National Formulary III. This concentration was carried on throughout the experiments except where otherwise indicated in the tables.

Practically every condition which usually affects the physical condition of precipitates has been given some study; some conditions more than others, according to the importance attached to them.

To more thoroughly understand the objects of these experiments a few desirable qualities of milk of magnesia will be enumerated:

## DESIRABLE QUALITIES OF MILK OF MAGNESIA.

*First.*—Reasonable uniformity in the percentage of magnesium hydroxide in the finished preparation.

*Second.*—Freedom from injurious foreign substances or undesirable by-products—heavy metals, arsenic, foreign alkalinity, and sodium and magnesium sulphates.

*Third.*—A non-separating magma, for the sake of pharmaceutical elegance only, a condition which is probably unobtainable.

*Fourth.*—Maximum fineness of the magnesium hydroxide and still retain fluidity of the preparation; this property is particularly desirable when milk of magnesia is to be used in infant feeding, where it is given more for its alkalinity than its laxative properties. It is axiomatic that the more surface of the magnesium hydroxide exposed to the milk the more rapidly will they react with each other. The importance of this last point may be understood by the fact that unmodified cows' milk is not readily digested by an infant unless its acidity is reduced by alkalies which produce a digestible curd. Cows' milk is about six times as acid as human milk; that is, cows' milk has 18 degrees acidity whereas human milk has only three.<sup>(1)</sup> To be useful in this respect the milk of magnesia must reduce the acidity before the milk enters the stomach. When cows' milk and milk of magnesia are mixed in the proper proportions to reduce the cows' milk to 3 degrees acidity it requires over six hours' contact. At 38° C. this is accomplished in about 35 minutes.

Some manufacturers advertise that their milk of magnesia is snow-white—this is a distinct disadvantage. The more opaque the milk of magnesia is, the less therapeutically active it is in any given time. The more translucent milk of magnesia is, the more desirable it is from a therapeutic standpoint.

Bearing these facts in mind and particularly the degree of fineness of the precipitate, the writers have endeavored to throw some light on the procedures required to produce as fine a preparation from a therapeutic and pharmaceutical standpoint as can be expected.

A series of experiments was performed as follows:

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\* Read before Section on Practical Pharmacy and Dispensing, A. Ph. A., New York meeting, 1919.

*Series No. 1.—MgSO<sub>4</sub> into NaOH.*

*Part A*—25° C.—MgSO<sub>4</sub><sup>1</sup> in excess—50-25-10%. Theoretical proportions, NaOH in excess—10-25-50%.

*Part B*—50° C.—MgSO<sub>4</sub> and NaOH in 10 percent excess and theoretical proportions.

*Part C*—100° C.—Same as Part B. (Nos. 1 to 13 inclusive.)

*Series No. 2.*

Same as Series No. 1, except NaOH into MgSO<sub>4</sub>. (Nos. 14 to 26 inclusive.)

*Series No. 3.—Solutions Double Concentrated.*

*Part A*—25° C.—MgSO<sub>4</sub> and NaOH in 10 percent excess and theoretical proportions.

*Part B*—50° C.—Same as A.

*Part C*—100° C.—Same as A. (Nos. 27 to 35 inclusive.)

*Series No. 4—25° C.*

*Part A*.—Same as Series No. 3, Part A, except solutions double dilute. (Nos. 36 to 38 inclusive.)

*Series No. 5—25° C.*

*Part A*.—Same as Series No. 3, Part A, except magnesium sulphate solution double concentrated. (Nos. 39 to 41 inclusive.)

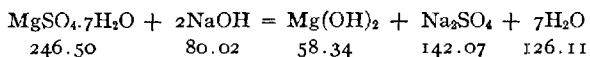
*Series No. 6—25° C.*

*Part A*.—Same as Series No. 3, Part A, except sodium hydroxide solution double concentrated. (Nos. 42 to 44 inclusive.)

By studying the various parts of Table I, which shows the degrees of fineness of the magnesium hydroxide as produced from the above series of experiments (value column), it will be noted that slight modification of some conditions materially affects the product. The value figures represent the height of the precipitate in millimeters after standing ten hours in a Nessler tube. The higher the number the more gelatinous the precipitate. For these experiments it was necessary to assume that the ratio in the speed of separation during the first ten hours will hold for any length of interval.

No experiments were performed on the U. S. P., or hydration process, as it has been shown that these procedures are not as valuable as the precipitation method.<sup>(2)</sup> A few experiments were performed using for the alkali potassium hydroxide and ammonium hydroxide. The potassium salt has no distinct advantage over the sodium salt, therefore, it would not prove popular, as it would increase the cost. Due to the solubility of magnesium hydroxide in ammonium hydroxide this substance is worthless.

The reaction is based on the following equation and the stoichiometric calculations were based on the atomic and molecular weights of the U. S. P. IX.



<sup>1</sup> Wherever the symbol "MgSO<sub>4</sub>" or the title "magnesium sulphate" appears in this paper it refers qualitatively and quantitatively to "MgSO<sub>4</sub>·7H<sub>2</sub>O" Mol. Wt. 246.50.

TABLE I.—SEPARATING VALUE OF MAGMAS.

*Part A.—Magnesium Sulphate Solution Poured into Sodium Hydroxide Solution.*

| No. | Constituent in excess.       | Percent excess. | Temp. ° C. | Value. |
|-----|------------------------------|-----------------|------------|--------|
| 1   | Magnesium Sulphate.....      | 50              | 25         | 146    |
| 2   | Magnesium Sulphate.....      | 25              | 25         | 138    |
| 3   | Magnesium Sulphate.....      | 10              | 25         | 107    |
| 4   | Theoretical Proportions..... | ..              | 25         | 65     |
| 5   | Sodium Hydroxide.....        | 10              | 25         | 70     |
| 6   | Sodium Hydroxide.....        | 25              | 25         | 106    |
| 7   | Sodium Hydroxide.....        | 50              | 25         | 168    |
| 8   | Magnesium Sulphate.....      | 10              | 50         | 178    |
| 9   | Theoretical Proportions..... | ..              | 50         | 122    |
| 10  | Sodium Hydroxide.....        | 10              | 50         | 60     |
| 11  | Magnesium Sulphate.....      | 10              | 100        | 183    |
| 12  | Theoretical Proportions..... | ..              | 100        | 126    |
| 13  | Sodium Hydroxide.....        | 10              | 100        | 96     |

*Part B.—Sodium Hydroxide Solution Poured into Magnesium Sulphate Solution.*

| No. | Constituent in excess.       | Percent excess. | Temp. ° C. | Value. |
|-----|------------------------------|-----------------|------------|--------|
| 14  | Magnesium Sulphate.....      | 50              | 25         | 176    |
| 15  | Magnesium Sulphate.....      | 25              | 25         | 215    |
| 16  | Magnesium Sulphate.....      | 10              | 25         | 101    |
| 17  | Theoretical Proportions..... | ..              | 25         | 93     |
| 18  | Sodium Hydroxide.....        | 10              | 25         | 92     |
| 19  | Sodium Hydroxide.....        | 25              | 25         | 90     |
| 20  | Sodium Hydroxide.....        | 50              | 25         | 90     |
| 21  | Magnesium Sulphate.....      | 10              | 50         | 85     |
| 22  | Theoretical Proportions..... | ..              | 50         | 94     |
| 23  | Sodium Hydroxide.....        | 10              | 50         | 107    |
| 24  | Magnesium Sulphate.....      | 10              | 100        | 117    |
| 25  | Theoretical Proportions..... | ..              | 100        | 110    |
| 26  | Sodium Hydroxide.....        | 10              | 100        | 111    |

*Part C.—Double Concentration of both Solutions. Magnesium Sulphate Solution Poured into Sodium Hydroxide Solution.*

| No. | Constituent in excess.       | Percent excess. | Temp. ° C. | Value. |
|-----|------------------------------|-----------------|------------|--------|
| 27  | Magnesium Sulphate.....      | 10              | 25         | 94     |
| 28  | Theoretical Proportions..... | ..              | 25         | 59     |
| 29  | Sodium Hydroxide.....        | 10              | 25         | 58     |
| 30  | Magnesium Sulphate.....      | 10              | 50         | 100    |
| 31  | Theoretical Proportions..... | ..              | 50         | 98     |
| 32  | Sodium Hydroxide.....        | 10              | 50         | 61     |
| 33  | Magnesium Sulphate.....      | 10              | 100        | 115    |
| 34  | Theoretical Proportions..... | ..              | 100        | 197    |
| 35  | Sodium Hydroxide.....        | 10              | 100        | 75     |

*Part D.—Double Dilution of both Solutions. Magnesium Sulphate Solution Poured into Sodium Hydroxide Solution.*

| No. | Constituent in excess.       | Percent excess. | Temp. ° C. | Value. |
|-----|------------------------------|-----------------|------------|--------|
| 36  | Magnesium Sulphate.....      | 10              | 25         | 118    |
| 37  | Theoretical Proportions..... | ..              | 25         | 120    |
| 38  | Sodium Hydroxide.....        | 10              | 25         | 166    |

*Part E.—Magnesium Sulphate Solution Double Concentrated. Magnesium Sulphate Solution Poured into Sodium Hydroxide Solution.*

| No. | Constituent in excess.       | Percent excess. | Temp. ° C. | Value. |
|-----|------------------------------|-----------------|------------|--------|
| 39  | Magnesium Sulphate.....      | 10              | 25         | 142    |
| 40  | Theoretical Proportions..... | ..              | 25         | 73     |
| 41  | Sodium Hydroxide.....        | 10              | 25         | 73     |

*Part F.—Sodium Hydroxide Solution Double Concentrated. Magnesium Sulphate Poured into Sodium Hydroxide Solution.*

| No. | Constituent in excess.       | Percent excess. | Temp. ° C. | Value. |
|-----|------------------------------|-----------------|------------|--------|
| 42  | Magnesium Sulphate.....      | 10              | 25         | 78     |
| 43  | Theoretical Proportions..... | ..              | 25         | 75     |
| 44  | Sodium Hydroxide.....        | 10              | 25         | 101    |

A few salient facts will be noted by Table I, Part A:

1. The greater the excess of magnesium sulphate the more gelatinous the precipitate.

2. When the magnesium sulphate is in 10 percent excess the gelatinization rises with the temperature. When the sodium hydroxide is in excess the temperature makes little difference. Theoretical proportion figures also rise with the temperature.

Part B, 1.—No definite generalization can be noted from the data.

Part C, 1.—By comparing the Nos. in part C with the corresponding ones in Part A it will be noted that the general effect of concentrating solutions is to decrease gelatinization.

Part D, 1.—By double dilution of both solutions the gelatinization is increased in every case.

In general, the more gelatinous precipitate is produced when the solutions are dilute and the temperature high. An excess of magnesium sulphate seems to produce a more gelatinous precipitate than when the sodium hydroxide is in excess. To account for all conditions it is necessary to study the tables carefully.

The densities of the supernatant liquids do not vary enough to materially affect the separation value. The densities varied from 1.010 to 1.015.

Another factor affecting the degree of gelatinization is the rapidity of mixing the solutions. Contrary to what might be expected the more rapidly the solutions are mixed the better the magma produced.

Table II gives analyses of the supernatant liquids from the different magmas, showing the adsorption of magnesium sulphate by the magnesium hydroxide. Each lot was diluted to 1002 mils and an aliquot portion analyzed. By diluting to 1002 mils, 100 mils will represent exactly one-tenth of the supernatant liquid, the 2 mils being the volume occupied by 5.9 Gm. magnesium hydroxide (specific gravity 2.84<sup>3</sup> as produced under average conditions).

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

In one case 1.2 percent of the total magnesium hydroxide consisted of magnesium sulphate held by<sup>3</sup> adsorption. In all cases where the alkali was in excess

<sup>3</sup> Van Nostrand's "Chemical Annual," 1918, gives specific gravity of Mg(OH)<sub>2</sub> as 2.36 at 15° C.

all the magnesium sulphate was precipitated, consequently none was adsorbed. There was no adsorption of sodium hydroxide under any of the conditions mentioned. Wherever the alkali was in excess the supernatant liquid required very close to the theoretical amount of standard acid for neutralization. This disproves the contention that an excess of magnesium sulphate is more easily washed out than an excess of alkali. It would seem that a slight excess of sodium hydroxide is to be preferred in the manufacture of this preparation by the retail pharmacist, who cannot assay his alkali, and base his calculations accordingly. One who is equipped for assaying may select his method, provided, of course, the finished product meets the official requirements.

TABLE II.—ADSORPTION OF MAGNESIUM SULPHATE AND SODIUM HYDROXIDE BY THE MAGNESIUM HYDROXIDE.

*Part A.—Magnesium Sulphate Solution Poured into Sodium Hydroxide Solution.*

NOTE.—In the following table under "Constituent in excess," Magnesium Sulphate has been abbreviated "Mg. S.," and "Theoretical Proportion, T. P."

| No. | Constituent in excess. | Percent excess. | Temp. ° C. | Mils. Sample. | Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . | Adsorbed. MgSO <sub>4</sub> ·7H <sub>2</sub> O. <sup>1</sup> | Mils. Sample. | N/10 H <sub>2</sub> SO <sub>4</sub> required. | N/10 H <sub>2</sub> SO <sub>4</sub> Theoretical. |
|-----|------------------------|-----------------|------------|---------------|---|--|---------------|---|--|
| 1   | Mg. S.                 | 50              | 25         | 50            | 0.2740  | 3.6750   | 100           | 0.55  | None   |
| 2   | Mg. S.                 | 25              | 25         | 50            | 0.1298  | 5.040  | 100           | 0.55  | None   |
| 3   | Mg. S.                 | 10              | 25         | 100           | 0.0941  | 4.170  | 100           | 0.55  | None   |
| 4   | T. P.                  |                 | 25         | 100           | 0.0034  | Trace  | 100           | 2.20  | None   |
| 5   | NaOH.                  | 10              | 25         | 100           | 0.0041  | Trace  | 25            | 5.10  | 5.07   |
| 6   | NaOH.                  | 25              | 25         | 100           | 0.0036  | Trace  | 25            | 12.74   | 12.64  |
| 7   | NaOH.                  | 50              | 25         | 100           | 0.0025  | Trace  | 25            | 25.10   | 25.36  |
| 8   | Mg. S.                 | 10              | 50         | 50            | 0.0566  | None   | 100           | 0.95  | None   |
| 9   | T. P.                  |                 | 50         | 100           | 0.0143  | None <sup>2</sup>  | 100           | 2.45  | None   |
| 10  | NaOH.                  | 10              | 50         | 100           | 0.0000  | None   | 25            | 4.30  | 5.07   |
| 11  | Mg. S.                 | 10              | 100        | 50            | 0.0538  | 1.1800   | 100           | 1.00  | None   |
| 12  | T. P.                  |                 | 100        | 100           | 0.0010  | Trace  | 100           | 2.40  | None   |
| 13  | NaOH.                  | 10              | 100        | 100           | 0.0000  | None   | 25            | 4.60  | 5.07   |

<sup>1</sup> Per 1000 mils of finished magma. <sup>2</sup> 3.1660 Gm. MgSO<sub>4</sub>·7H<sub>2</sub>O not precipitated.

*Part B.—Sodium Hydroxide Solution Poured into Magnesium Sulphate Solution.*

| No. | Constituent in excess.   | Percent excess. | Temp. ° C. | Mils. Sample. | Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> . | Adsorbed. MgSO <sub>4</sub> ·7H <sub>2</sub> O. <sup>1</sup> |
|-----|--------------------------|-----------------|------------|---------------|---|--|
| 14  | Magnesium Sulphate.      | 50              | 25         | 50            | 0.2269  | 2.4560   |
| 15  | Magnesium Sulphate.      | 25              | 25         | 50            | 0.0833  | 2.5640   |
| 16  | Magnesium Sulphate.      | 10              | 25         | 100           | 0.0020  | Trace  |
| 17  | Theoretical Proportions. |                 | 25         | 100           | Trace   | Trace  |
| 18  | Sodium Hydroxide.        | 10              | 25         | 100           | 0.0000  | None   |
| 19  | Sodium Hydroxide.        | 25              | 25         | 100           | 0.0000  | None   |
| 20  | Sodium Hydroxide.        | 50              | 25         | 100           | 0.0000  | None   |

<sup>1</sup> Per liter of finished magma.

BIBLIOGRAPHY.

<sup>1</sup> Terry, R. W., "Potential Acidity of Milk and a Standard Method for its Determination," J. A. PH. A., July 1919, p. 583.

<sup>2</sup> Terry, R. W., "Analyses of Milk of Magnesia," J. A. PH. A., March 1919, p. 183.

ABSTRACT OF DISCUSSION.

OTTO RAUBENHEIMER: In my opinion the change to the present official formula was a mistake; also the increase in strength from 5 to 7½ percent. Milk of magnesia should be a smooth colloidal magma; it is not necessary to have it very thick. I hope that the new official method for making milk of magnesia will be by precipitation.

R. W. TERRY: In my paper of last year on the analyses of different brands of milk of magnesia, I pointed out the deficiencies in various formulas and that in the U. S. P. and N. F. formulas there was not sufficient alkali to precipitate all the magnesia. In the present paper the chemistry of the precipitation of magnesium hydroxide has been studied. Next year, I hope to be able to present some definite formulas for milk of magnesia.

L. E. SAYRE: Did the author report relative to the rapidity of precipitation?

R. W. TERRY: Yes, the more rapid the mixing the better the magma produced.

C. S. HERRON: My experience in making milk of magnesia is with 500-gallon lots. We use a 70 percent caustic with which a solution of a 1.17 specific gravity is made. The solution of magnesium sulphate is also of the same density. After precipitation, live steam is passed through the magma for about three hours. When the washing is completed the magma is free from sulphates. We have found that the specific gravity of the solutions is an important factor.

L. E. SAYRE: There is quite a variability in these magnesia preparations so far as the presence of sulphates in them is concerned.

Mr. Terry was questioned relative to certain qualities that milk of magnesia should possess. These questions were answered in the paper under the sub-head of "Desirable Qualities of Milk of Magnesia," hence, this part of the discussion is omitted.—The EDITOR.

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## THE ABUSE OF THE "SHAKE-WELL LABEL," WITH DEMONSTRATIONS.\*

BY J. LEON LASCOFF.

The dispensing pharmacist frequently comes across difficult prescriptions, especially in the form of mixtures which do not contain insoluble matter. Unfortunately, being very busy with his routine work, very little or no attention is paid to such prescriptions. He mixes the constituents in the order written, does not consult any book of reference, and finds an easy way to overcome this need by the use of the "Shake-well Label," which he places on the bottle.

When this same prescription is dispensed in another store where the pharmacist prepares it scientifically the finished product is without a heavy sediment, transparent or a clear solution, and does not bear the so-called "Shake-well Label," used by the former pharmacist.

The abuse of the "Shake-well Label," by being placed on every mixture, has been practiced for some time. I do not mean to imply that we should do away entirely with these labels; on the contrary, sometimes even in clear solutions (in a mixture of an alkaloid and an alkali) it is absolutely essential to have such label on the bottle.

During the last two decades committees on propaganda were organized, for the purpose of holding joint meetings of the allied professions and to urge the medical men to prescribe combinations of their own, instead of the so-called proprietary articles.

The further object of these meetings is to prove to the physicians that we have scientific pharmacists who take an interest and pride in their work—and that is dispensing.

At the June meeting of the New York State Pharmaceutical Association President Smith, in his annual address, classified pharmacy as follows:

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\* Read before Section on Practical Pharmacy and Dispensing, A. Ph. A., New York meet-