

These concentrations were selected as those most used in the medical application of these products.

The results of this work have been calculated to p_{Ag} values and also in mols of ionized Ag per liter. They are given in the following table.

		0 day.	1 day.	2 days.	1 week.	1 month.	4 months.	16 months.
Strong	A	p_{Ag} 2.08	2.05	2.05	2.20	2.74	2.93	3.39
		M Conc. 8.3×10^{-3}	8.9×10^{-3}	8.9×10^{-3}	6.3×10^{-3}	1.8×10^{-3}	1.2×10^{-3}	4.1×10^{-4}
	B	p_{Ag} 2.13	2.15	2.12	2.13	2.76	3.10	3.88
		M Conc. 7.4×10^{-3}	7.1×10^{-3}	7.6×10^{-3}	7.4×10^{-3}	1.7×10^{-3}	8.0×10^{-4}	1.3×10^{-4}
	C	p_{Ag} 3.51	3.45	3.45	3.51	4.32	4.88	5.62
		M Conc. 3.1×10^{-4}	3.5×10^{-4}	3.5×10^{-4}	3.1×10^{-4}	4.8×10^{-5}	1.3×10^{-5}	2.4×10^{-6}
Mild	A	p_{Ag} 6.68	6.92	6.78	6.89	7.20	7.17	6.92
		M Conc. 2.1×10^{-7}	1.2×10^{-7}	1.7×10^{-7}	1.3×10^{-7}	6.3×10^{-8}	6.7×10^{-8}	1.2×10^{-7}
	B	p_{Ag} 7.88	8.46	6.98	7.00	7.63	7.27	5.57
		M Conc. 1.3×10^{-8}	3.5×10^{-9}	1.1×10^{-7}	1.0×10^{-7}	2.3×10^{-8}	5.4×10^{-8}	2.7×10^{-8}
	C	p_{Ag} 7.25	7.79	8.12	7.79	8.32	7.88	5.85
		M Conc. 5.6×10^{-9}	1.6×10^{-8}	7.6×10^{-9}	1.61×10^{-8}	4.8×10^{-9}	1.3×10^{-8}	1.4×10^{-6}
	D	p_{Ag} 12.90	12.84	12.70	12.72	13.75	13.94	13.79
		M Conc. 1.3×10^{-13}	1.4×10^{-13}	2.0×10^{-13}	1.9×10^{-13}	1.8×10^{-14}	1.2×10^{-14}	1.7×10^{-14}
	E	p_{Ag} 12.98	12.80	13.02	12.85	13.77	13.89	14.02
		M Conc. 1.1×10^{-13}	1.6×10^{-13}	9.6×10^{-14}	1.4×10^{-13}	1.7×10^{-14}	1.3×10^{-14}	9.6×10^{-15}

The solutions of compounds of the strong type show an almost uniform loss in silver ions in aging. The solutions of materials of the mild type do not in general show any consistent trend. Samples B and C of the mild type show first a decrease and in the last readings an increase in silver ions over the original value. Sample A of the mild type shows the least variations of any of this class and in general shows a more or less regular tendency toward a decrease in silver-ion concentration.

The two compounds of the mild type in which the silver-ion concentration is low show in the first few days a slight increase in silver-ion concentration which is followed by a decrease in the ion concentration over the rest of the time of storage.

Conclusions.—The changes in silver-ion concentration which take place in solutions of colloidal silver compounds within the first month are negligible and those occurring in the first four months are not believed to be great enough to cause any change in the germicidal power.

If any of these solutions on aging, produces irritation, it must be due to changes in the solution other than silver-ion concentration.

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COLLOIDAL BARIUM SULPHATE.*

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Colloidal preparations are becoming increasingly interesting from the point of view of their usefulness in the practice of medicine, and the study of their therapeutic properties and of their preparation is becoming a much attended field of pharmaceutical research.

* Scientific Section, A. P. H. A., St. Louis meeting, 1928.

It is obviously possible to market these preparations in either of two forms, *viz.*, in a dry form which, when admixed with water or another medium, will be quickly dispersed; or, in the form of the dispersion in the proper medium. The latter method entails the disadvantage of bulk, and usually that of gradual deterioration due to growth and partial precipitation of the particles.

Unfortunately, there are only a few substances which, when in colloidal form, can be dried and then redispersed or reprecipitated by simple admixture with the dispersion medium. These reversible colloids are the highly hydrated or hydrophylic colloids, as for example gelatin, gum arabic and pectin. The irreversible colloids, which cannot be reprecipitated after drying, are the slightly hydrated or hydrophobic colloids, as for example, the colloidal metals, salts and the more basic metal oxides. There should be recognized also, a middle class of considerably hydrated colloids comprising the more acidic oxides, *i. e.*, Fe_2O_3 and SiO_2 , which can be reprecipitated if not quite completely dried. It may also be remarked that often an irreversible colloid can be made reversible if it be dried with the proper proportion of a reversible colloid.

It occurred to the author that the mechanism whereby an irreversible colloid is converted to the crystalloidal state while being dried might be interfered with and thus allow the substance to remain colloidal up to the point of complete dehydration. Once in the condition of a dry powder, certainly no further change would occur, and reprecipitation should be possible. This change to the crystalloidal state would occur through growth of particles and loss of electrical charge. We believe that, until that particle size is reached, above which no difference in solubility due to difference in particle size exists (about 2μ for CaSO_4) the growth of particles is due almost entirely to the process of redissolving of the smaller particles and redeposition upon the larger particles, and not to agglomeration. This process of growth of the larger particles at the expense of the smaller ones is a familiar one and has been discussed by Ostwald,¹ and by Hulett.² The latter states that coarsely crystalline BaSO_4 (1.8μ) dissolves to the extent of 2.29 mg. per liter at 25°C. , while particles 0.1μ dissolve to the extent of 4.5 mg. per liter. This process ought to be retarded, therefore, if either the rate of solution or the solubility of the colloid is decreased. This can be accomplished by,

1. Keeping the temperature low.
2. Keeping the total quantity of solvent at a minimum.
3. Mixing an organic solvent such as alcohol with the water.
4. Decreasing the time of exposure to the solvent by drying in vacuum.

Von Weimarn had used the conditions of high concentration and addition of alcohol for the preparation of colloidal BaSO_4 .

It was decided to attempt to prepare BaSO_4 as a reversible colloid by setting up these conditions, during the preparation and the drying process; BaSO_4 was chosen because it is extremely hydrophobic, is very insoluble, and might be of greater value in x-ray work if prepared as a reversible colloid, since it would be more readily suspended, and give a longer period of opacity due to its greater resistance to settling.

¹ *Z. physik. Chem.*, 35 (1900), 495.

² *Ibid.*, 37 (1901), 385.

EXPERIMENTAL.

I. Sixty Gm. of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ were moistened with water to form a paste. To this was added glacial acetic acid until neutral to phenolphthalein. This concentrated solution of BaAc_2 was cooled to 65°C .; 16.2 Gm. 96% H_2SO_4 were diluted with 65 Gm. of alcohol and cooled to 0°C .

The H_2SO_4 solution was now added to the BaAc_2 solution while stirring rapidly. The resulting colloidal solution was dried in a vacuum desiccator at 60°C . The dried BaSO_4 was readily reprecipitated with water. The colloidal solution passed completely through a No. 5 Whatman filter and remained stable for several days.

II. Fifty Gm. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 75 cc. H_2O were cooled to 5°C . while stirring so that the crystals that form will remain small; 20.9 Gm. 96% H_2SO_4 were dissolved in 75 cc. ethyl alcohol and the solution cooled to 0°C . The acid was added to the barium-chloride solution while stirring rapidly. The colloidal solution was dried at 65°C . in vacuum, and was reversible.

III. Sixty Gm. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ were dissolved in 75 cc. hot water, and cooled to about 10°C . very rapidly, while stirring. Small crystals formed; 18.66 Gm. 96% H_2SO_4 dissolved in 75 cc. alcohol were cooled to 0°C ., and poured into the $\text{Ba}(\text{OH})_2$ paste while stirring. The colloid was dried as before and proved to be reversible.

The best results were obtained with the acetate.

In every case where the colloid proved to be reversible, a small excess of soluble barium salt was detected in the colloid by the U. S. P. test. The products were, however, no more toxic to white rats or guinea-pigs than ordinary precipitated BaSO_4 , which indicates that the soluble Ba^{xx} ion was strongly adsorbed in the surface of the micellæ rather than in free solution. This was further attested to by the fact that throughout a large number of trials, no material remained colloidal if the Ba^{xx} ion was completely converted to the sulphate. This shows that the colloid is peptized by the adsorbed Ba^{xx} ions, and that without them the particles are immediately agglomerated. It is for this reason that poor results are obtained when the barium salt is added to the sulphate, instead of vice versa, for in only the latter case is the Ba^{xx} always in excess during the formation of the colloid.

SUMMARY.

1. A hydrophobic colloid was made reversible without the admixture of a hydrophylic colloid.

2. It is indicated that growth of particles is almost entirely by the resolution of smaller particles and redeposition upon the larger particles while the particles are below that size above which there is no further variation in solubility due to difference in the size of particles; unless the particles are not charged electrically. After this size has been attained, and if the particles below that size are discharged, growth of particles is probably by agglomeration.

3. Insufficient work was done in order to determine the optimum excess of soluble Ba^{xx} , but it was found that a small excess was necessary.