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MANUFACTURE OF HYDRATED POLYSILICATE

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8 Claims. (Cl. 23—110)

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This invention relates to manufacture of hydrated polysilicate; and it comprises as a new product, the compound $Na_2O:4.4SiO_2$ in hydrated crystalline form; said product occurring in the form of white, fluffy crystals having a diameter ranging from about 1 to 10 microns and containing about 3 molecules of water of crystallization. The invention further comprises processes of manufacturing said hydrated sodium tetrasilicate comprising seeding concentrated sodium silicate solutions of high silica ratio with seed crystals of said tetrasilicate and advantageously maintaining said solutions at elevated temperatures favoring crystal growth and under conditions of agitation; all as more fully hereinafter set forth and as claimed.

While several crystalline hydrates of sodium metasilicate and at least one crystalline hydrate of sodium sesquisilicate have been reported in the literature, up until the time of the present invention no crystalline hydrates containing more than 2 moles of SiO_2 to 1 mole of Na_2O have been isolated at ordinary temperatures. In the phase rule system consisting of Na_2O, SiO_2 and H_2O, our knowledge of the field which includes high silica ratios is very limited.

We have now discovered a new crystalline hydrate having a ratio of Na_2O to SiO_2 which lies between about 1:4.3 to 1:4.5, the value determined by analysis depending upon the method and accuracy of the analytical method employed, and containing from about 2 to 4 molecules of water of hydration. We have further found methods of preparing this compound and have developed various uses to which it may be put.

The new compound can be prepared from concentrated solutions of sodium silicate having high ratios of silica. It is best formed at elevated temperatures although it can be prepared at a slower rate at ordinary temperatures or below. The rate of formation is greatly accelerated by heating and by agitation. Increased temperatures reduce the viscosity of the sodium silicate solutions and this may account for the increased speed of crystal formation. By using the word "compound" in describing our new product, we do not intend to exclude the possibility that this new product is a solid solution although our experimental results do not indicate that such is the case.

It has been found somewhat difficult to promote spontaneous formation of the tetrasilicate crystals. Our experiments indicate that spontaneous formation can be accomplished, with a small yield of crystals, in a period of two or more months, if a solution containing 11 per cent Na_2O and 32 per cent SiO_2 is agitated and heated to temperatures of about 75° to 85° C. over such a period of time. We have found that it usually requires several years for the spontaneous formation of tetrasilicate crystals to occur in the same solution standing at room temperatures. When seed crystals are added to solutions capable of growing the crystals, however, propagation can be accomplished at a reasonable rate of speed provided operating conditions are properly chosen.

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Our experiments indicate that the tetrasilicate crystals can be grown in any concentrated liquid silicate solution of high silica ratio containing the proper proportion of water and advantageously having a ratio of Na_2O to SiO_2 ranging from about 1:2 to 1:11 or above. Best results have been obtained when the SiO_2 in this ratio has been above 2.4. The amount of water present should not exceed about 75 to 80 per cent by weight. As examples of solutions which are capable of growing crystals of the new tetrasilicate, there may be mentioned the following six sodium silicate solutions which have been employed in practice in growing tetrasilicate crystals, these solutions containing Na_2O and SiO_2 in the precentages by weight as indicated: (1) 6.0% Na_2O, 23.6% SiO_2; (2) 6.3% Na_2O, 22.9% Sio_2; (3) 8.3% Na_2O, 24.0% SiO_2; (4) 9.4% Na_2O, 23.8% SiO_2; (5) 11.0% Na_2O, 26.6% SiO_2; (6) 13.7% Na_2O, 32.9% SiO_2. The percentages of water in these solutions can be found by subtracting the percentages of Na_2O and SiO_2 from 100%. Our experiments indicate that temperatures ranging from about 0° to 100° C. can be employed in growing tetrasilicate crystals although we have obtained best results within the narrower range of from about 60° to 90° C.

In preparing the tetrasilicate crystals it is merely necessary to prepare a suitable sodium silicate solution, to add seed crystals thereto and then to allow the solution to stand for a sufficient length of time either at room temperatures or above. The growth of the crystals can be accelerated by heating the solution to temperatures somewhat below 90° C. and by agitation. The optimum crystallizing temperature appears to be between about 75° and 85° C. but even at this temperature it usually requires several days for the seed crystals to double in weight. The resulting magma of crystals may be separated from the mother liquor by filtration or by the use of a centrifuge, for example, and then washed with water. Since the crystals dissolve very

slowly at ordinary temperatures they may be washed thoroughly if cold water is used. The crystals should then be dried at temperatures which are advantageously below 80° C., since under ordinary conditions they lose water rather rapidly above this temperature.

In order to dry the crystals rapidly they may be washed with any convenient water-soluble volatile solvent which will not react with the crystals. Alcohol followed by ether may be used although our experiments show that alcohol reacts to some extent with the crystals to form a gel coating.

The tetrasilicate crystals are usually obtained in extremely finely divided form. When examined under a low power microscope it is difficult to distinguish the shape of the crystals although their birefringence is plainly noticeable. The crystals usually vary in diameter from about 1 to 10 microns. When examined as to their optical properties it has been found that the crystals are either uniaxial or, if biaxial, β and γ are practically identical. The elongation is γ, extinction parallel. α equals $1.463 \pm .003$. γ equals $1.483 \pm .003$.

The crystals are stable in their mother liquor for periods of longer than one month when frozen in ice. They are also stable in solutions kept at 85° C. and have been kept at 95° C. for five hours with only partial solution. The mother liquor used in these particular tests analyzed 9.38 per cent Na_2O, 25.41 per cent SiO_2 and 65.16 per cent H_2O.

Our experiments show that the tetrasilicate crystals lose water on heating, even at fairly low temperatures. When dried at 62° C. for example, they retain from about 13 to 17 per cent of water. Heated at 80° C. there is an additional loss of a little over 1 per cent of water. After drying at 100° C. there is somewhat less than 6 per cent of water remaining, while at 320° C. there still remains about 1.5 per cent of water. These experiments indicate the existence of several hydrates of the composition $Na_2O:4.4SiO_2:xH_2O$, having transition points lying between the temperatures of 0° to 200° C. or above. The present invention provides methods of preparing such hydrates.

In obtaining proof of the chemical composition of the new crystals, several different methods of analysis were employed. Employing the so-called "inert material method" (described in "Treatise on Physical Chemistry" by Hugh S. Taylor, D. Van Nostrand Co., Inc., New York, 2nd edition (1931), vol. I, page 560, last paragraph) for estimating the amount of mother liquor mixed with the crystals, we used sodium chloride as the inert material. In one analysis by this method we found the molecular ratios of $Na_2O:SiO_2:H_2O$ to be 1:3.97:7.00, while in a second test, in which a larger quantity of mother liquor was mixed with the crystals, we obtained ratios of 1:4.09:7.57. Since the latter results included a greater experimental error due to the larger amount of mother liquor, the former values of the ratios are probably the more nearly correct. A direct analysis of the crystals, after washing with water to free them from mother liquor, gave a ratio of Na_2O to SiO_2 of 1:4.00. Three more recent analyses by the inert material method, using an improved technique in which the inert material was present during the growth of the crystals and which therefore took account of any

mother liquor inclusions in the crystal masses, gave values of $1Na_2O:4.2SiO_2:3.9H_2O$;

$$1Na_2O:4.1SiO_2:3.7H_2O$$

and $1Na_2O:4.2SiO_2:4.2H_2O$, respectively.

The above results were also checked by the so-called wet residue method of Schreinemaker, described in Z. Physikal. Chem., 11, 76 (1893). In these tests four sodium silicate solutions of different composition were prepared and tetrasilicate crystals were grown in each. The mother liquors and the wet residue of crystals were then analyzed. These data were then used, according to the method of Schreinemaker, to estimate the percentages of Na_2O present in the dry crystals. The results obtained for the four solutions gave percentages of 14.09%, 14.18%, 13.91% and 14.30%, respectively, for the Na_2O present in the dry crystals. This compares with a theoretical value of 14.47% Na_2O for the compound $Na_2O:4SiO_2:7H_2O$.

A number of more recent analyses by the wet residue method, using an improved technique in which the probable accuracy was about double that obtained in tests mentioned in the preceding paragraph, indicate that the composition of the new product lies between about

$$1Na_2O:4.5SiO_2:2H_2O$$

and $1Na_2O:4.3SiO_2:3.7H_2O$. A series of analyses involving the steps of washing and pressing a magma of crystals between filter paper, followed by analysis of the pressed residue, indicates that the composition is between the values

$$1Na_2O:4.3SiO_2:3.7H_2O$$

and $1Na_2O:4.5SiO_2:3.5H_2O$. Experiments involving drying a washed magma of crystals to constant weight followed by analysis, gave values indicating an average composition of

$$1Na_2O:4.5SiO_2:2H_2O$$

The above data indicate that the crystals of the present invention correspond to a tetrasilicate having a composition lying between about $1Na_2O:4.3SiO_2:2H_2O$ and $1Na_2O:4.5SiO_2:4H_2O$, or, as an average value, $1Na_2O:4.4SiO_2:3H_2O$. Of course the most accurate way of identifying crystalline compositions is by measurement of the refractive index of the crystals. These measurements have been made many times on different samples of our composition without finding any deviation from the crystal constants set out above. X-ray diffraction patterns have also been made on several different samples but no indication has been found that different crystal phases were present. From this it is concluded that we are dealing with a single crystal phase the chemical analysis of which is doubtless fixed but difficult to determine with accuracy.

In one specific embodiment of the process of the present invention we took 29 kilograms of a silicate of soda solution containing 11 per cent Na_2O and 33 per cent of SiO_2. We seeded this solution with a magma of crystals of tetrasilicate recovered from a previous operation weighing 3.25 kilograms and containing 22 per cent crystals, i. e. 715 grams dry weight. This solution was stirred at high speed and maintained at a temperature of 80° C. for 24 hours. The tetrasilicate crystals were recovered from this solution, washed and dried, with a yield of 1,199 grams, representing 484 grams, dry weight, of crystals grown. There was a loss of weight by evaporation of the solution amounting to about

10 per cent. The liquid silicate going into the formation of the crystals amounted to 1.55 per cent.

In another operation we took 21 kilograms of the same silicate of soda solution and added a crystal sludge weighing 3.83 kilograms or 843 grams of crystals, dry weight. This mixture was agitated, but at a slower rate than in the preceding example, for a period of 7 days while the temperature was maintained at 70° C. In this case the dry weight of the crystals grown was 149 grams. The loss by evaporation amounted to about 10 per cent and the liquid silicate forming the crystals amounted to 0.6 per cent.

Our new tetrasilicate has characteristics which adapt it to many uses. Some of the uses for which it appears particularly adapted are as follows:

(1) As an ingredient for enamels adapted to provide silica in a readily fluxible form to make possible a high silica content in the enamel without release of gas.

(2) As an ingredient of cements and concretes where a slowly soluble silica is desirable as a hardening agent, or where silica in more reactive form than pure quartz is required.

(3) As a means of purifying silicates and of obtaining highly siliceous silicates in pure form without the cost and danger of contamination inherent in the fusion process, and having the advantage of a fine state of subdivision without the need of grinding and consequent contamination from that source.

(4) As a finely divided product which combines abrasives and cleansing properties either alone or as an ingredient of cleansing compositions.

It is likewise evident that the tetrasilicate can be employed in making up silicate solutions, that caustic soda can be added to these solutions to vary the ratio of Na_2O to SiO_2 and that the resulting solutions can be employed for all the various uses which have been suggested previously for silicate solutions of similar compositions.

While we have described what we consider to be the best embodiments of our invention it will be obvious to those skilled in the art that various modifications can be made in the procedure outlined. Our new tetrasilicate can be prepared over a considerable range of conditions or, more specifically, over those ranges of temperature, concentration, pressure, etc. from which the crystalline compound having the described properties will separate as a solid phase in contact with mother liquor, as understood under the principles of the phase rule. Modifications of our method which fall within the scope of the following claims we consider to be part of our invention.

What we claim is:

1. A crystalline product composed of fine crystals whose elongation is γ, extinction parallel and wherein α equals $1.463 \pm .003$, and γ equals $1.483 \pm .003$; said crystals having a molecular ratio of Na_2O to SiO_2 of from 1:4.3 to 1:4.5 and containing approximately 2 to 4 molecules of water.

2. In the process of manufacturing crystalline silicates, the step which comprises seeding a sodium silicate solution, containing more SiO_2 than is represented by the molecular ratio of $1Na_2O$ to $2SiO_2$ and containing not substantially more than about 75 per cent of water, with

crystals having a molecular ratio of Na_2O to SiO_2 of from about 1:4.3 to 1:4.5 and containing approximately 2 to 4 molecules of water.

3. The process which comprises seeding a concentrated sodium silicate solution, having a molecular ratio of SiO_2 to Na_2O above about 2 to 1, with crystals having a molecular ratio of Na_2O to SiO_2 of from about 1:4.3 to 1:4.5 and containing approximately 2 to 4 molecules of water, and heating said solution within a temperature range of from about 60° to 90° C. for a time sufficient to grow said crystals.

4. The process which comprises adding crystals, having a molecular ratio of Na_2O to SiO_2 of from about 1:4.3 to 1:4.5 and containing approximately 2 to 4 molecules of water, to a concentrated sodium silicate solution containing SiO_2 in amount greater than that represented by the molecular ratio of $1Na_2O$ to $2SiO_2$ and agitating the solution while maintaining conditions favorable for the growth of said crystals.

5. The process which comprises adding crystals, having a molecular ratio of Na_2O to SiO_2 of from about 1:4.3 to 1:4.5 and containing approximately 2 to 4 molecules of water, to a concentrated sodium silicate solution containing SiO_2 in amount greater than that represented by the molecular ratio of $1Na_2O$ to $2SiO_2$, agitating said solution and heating it to temperatures below about 100° C. for a time sufficient to grow said crystals.

6. The process which comprises adding crystals, having a molecular ratio of Na_2O to SiO_2 of from about 1:4.3 to 1:4.5 and containing approximately 2 to 4 molecules of water, to a sodium silicate solution having a ratio of Na_2O to SiO_2 ranging from about 1:2.4 to 1:11 and maintaining said solution within the temperature range of about 75° to 85° C. and under conditions of agitation for a time sufficient to grow said crystals.

7. The process which comprises heating a sodium silicate solution containing SiO_2 in amount greater than that represented by the molecular ratio of $1Na_2O$ to $2SiO_2$ to temperatures ranging from about 60° to 90° C. under conditions of agitation for a time sufficient to grow crystals having a molecular ratio of Na_2O to SiO_2 of from about 1:4.3 to 1:4.5 and containing about 2 to 4 molecules of water.

8. The process which comprises heating crystals, having a molecular ratio of Na_2O to SiO_2 of from about 1:4.3 to 1:4.5 and containing approximately 2 to 4 molecules of water, under conditions producing loss of water, thereby preparing compounds having the proximate composition $Na_2O:4.4SiO_2:xH_2O$, wherein x is less than 7.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Certificate of Correction

Reissue No. 23,043. October 5, 1948.

WALTER F. WEGST ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 6, line 56, claim 8, after the word "compounds" insert *containing water of hydration and*; line 58, same claim, for the numeral "7" read *4*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 22nd day of February, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.