

The Control of the Pore Volume and Pore Size Distribution in Alumina and Silica Gels by the Addition of Water Soluble Organic Polymers*

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Received August 16, 1962

A method is described for preparing alumina and silica gels containing a controlled and enlarged pore volume distribution by the addition of water soluble organic polymers. Mixtures of hydrous gel and polymer were prepared in two ways: by precipitating the gel from solutions containing the dissolved organic matter; and by dispersing the polymer in the hydrous gel after the precipitation step. The organic matter was carried through the drying process until the structure set then calcined out of the system. It was found that polymers such as (a) the polyethylene glycols and polyethylene oxides bring about a large increase in the pore volume in the pore size range 1000 to 20 Å radius, (b) the methyl cellulose compounds form mainly large pores, and (c) polymers such as the polyvinyl alcohols and the polyacrylamides increase the pore volume across the entire pore size range 10³ to 20 Å radius. The pore volume distribution, surface area, and apparent bulk density data are given for typical gels made with each type of polymer. The volume distribution measurements were made by the method of mercury penetration and the surface areas measured by the nitrogen adsorption technique.

INTRODUCTION

The purpose of the present investigation was to establish a method for obtaining a controlled pore size distribution and an enlarged pore volume in inorganic gels such as silica and alumina gel or mixtures of the two. The pore volume contained in silica and alumina gels prepared by conventional methods is, in general, of the order of 0.3 to 0.8 ml/g of solid. Under certain circumstances, the pore volume can be varied by changing the concentrations

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of the reagents used to prepare the gel or by changing the time and temperature conditions of its preparation (1). However, there are very definite limits to the extent to which the pore volume can be increased or decreased by changes of this type. To obtain an additional measure of control over the pore size distribution and pore volume, water soluble organic polymers were added to the gels in the course of their preparation, carried through the preliminary drying process until the structure set, and finally were calcined out of the system at 500–600°C. The water soluble polymers that have been found to be exceptionally good for this purpose are the polyethylene glycols, polyvinyl alcohols, polyacrylamides, and the methyl cellulose compounds.

The inclusion of organic matter in gels to bring about changes in the density or "porosity" is a technique that has been used before. In some cases the organic mat-

ter has been added before the precipitation process (2), in others, afterwards (3). Some investigators have washed the organic matter out of the dried gel (4), others have calcined it out (2, 3), still others sublime or distill it out (5, 6). These previous investigations, however, were seriously restricted by two factors: (a) the limited solubility of the polymers available, and (b) the difficult task of measuring the pore volume distribution and estimating the changes brought about by the organic matter. In the previous studies polymers of natural origin (gelatin, gum arabic, etc.) were all that could be obtained in reasonable quantities. During the last decade synthetic polymers, such as those mentioned earlier, with comparatively large solubilities in water have come into widespread use. The physical properties of the calcined gel that were measured were usually the density or the surface area. While these properties are an indication of the type of changes that take place, they do not reflect accurately the changes in the pore size distribution. The approach taken in the present study was to combine the availability of highly soluble polymers and a much improved technique for measuring the pore volume distribution, the high pressure mercury penetration technique proposed by Ritter and Drake (7).

Experiments have been made to determine the nature and extent of changes in the pore structure brought about by various types of polymers and the best method of forming the mixture of gel and polymer. Efforts have also been made to determine the principle whereby certain additives function with the view to predicting the action of other polymeric materials. High pressure mercury porosimetry measurements are both difficult and costly. Where feasible, all pore volume measurements and effects of additives have been correlated with standard laboratory bulk density measurements. Future investigators wishing to make gels with the characteristics we describe can do so using the procedures described in this work with density measurements as a laboratory control.

EXPERIMENTAL

The Preparation of the Samples of Gels

Water soluble organic polymers were added to three types of gels: alumina gel, silica gel, and a co-precipitated alumina-silica gel containing approximately 6% SiO_2 (dry basis). The mixtures of gel and polymer were prepared in two ways:

(a) by dissolving the organic matter in the solutions used to make the gel and precipitating the gel in the presence of the additive, and

(b) by dissolving or dispersing the additive in the hydrous mass of gel after it had been precipitated, washed, and filtered.

There is a variety of ways in which the concentration of polymer added to the system can be expressed. Chiefly because the molecular weight data for many of the polymers were incomplete, the "weight per cent" method was adopted based upon the total *starting* weight of the system. In the case where the organic matter was added before precipitation, the concentration of polymer is expressed as a weight per cent of the combined weight of the solutions used, i.e., water, salts, and additive. Where the organic matter was added to the hydrous mass of gel after the precipitation process, the concentration of additive is expressed as a weight per cent of the combined weight of hydrous gel and polymer.* In the sections that follow a description is given of the reagents, concentrations, and drying procedures used for each type of gel. The recipes used were based upon those published by Ciapetta and Plank (8). For those gels prepared with the organic matter dissolved in the solutions prior to precipitation, the required amount of polymer was dissolved in a portion of the water called for in the recipe. Where the organic matter was added to the filtered, hydrous gel, the required amount of polymer was blended into the gel using a beater type stirrer; the mixture was then allowed to

*The percentage calculated in this way was always less than 100. If the calculations had been based upon the weight of oxide gel finally obtained, the concentration would be in hundreds or thousands of per cent.

stand overnight before beginning the drying procedure.

Alumina gel.

Solution 1: 100 g of reagent grade $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in distilled water to form 1 liter of solution.

Solution 2: 300 ml of concentrated ammonium hydroxide diluted with water to form 2 liters of solution.

The gel was precipitated by adding Solution 1 to Solution 2 as quickly as possible with vigorous stirring at room temperature. After precipitation the stirrer was kept in operation in the slurry for 10 min. The precipitate was then allowed to settle (usually overnight), the bulk of the liquid decanted, and the remaining liquid removed in a stainless steel pressure filter. The filter cake was dried at approximately 130–140°C for 24 hr and then calcined at 550–600°C for 3 to 4 hr (or until no carbon residue remained).

Silica gel.

Solution 3: 250 ml of water glass (Philadelphia Quartz Co. type N water glass, 28.7% SiO_2 and $\text{Na}_2\text{O}:\text{SiO}_2 = 1:3.22$) diluted with 687 ml of water.

Solution 4: 150 ml 4 N HCl diluted to 628 ml with water.

The gel was prepared by adding solution 4 to solution 3 as quickly as possible with vigorous stirring at room temperature. The combined solutions were poured into a glass tray to set and to age overnight. The gel was then cut into $\frac{3}{4}$ -inch cubes, placed in a Soxhlet type extraction flask and exchanged with 1 N HCl for 6 hr and finally washed with distilled water for 18 hr. The exchanged and washed gel was dried in an oven at 200°C for 24 hr and calcined at 550–600°C for approximately 4 hr.

Alumina-silica gel.

Solution 5: 100 g of reagent grade $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in distilled water to form 1 liter of solution.

Solution 6: 300 ml of concentrated ammonium hydroxide and 8.3 g of reagent grade $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ diluted and dissolved to form 2 liters of solution.

The gel was precipitated by adding Solution 5 to Solution 6 as quickly as possible, with vigorous stirring at room temperature. The stirrer was kept in operation in the slurry for approximately 10 min; then the gel was allowed to settle, and was finally filtered in the same way as the pure alumina gels. To remove any entrained sodium, the filter cake was slurried with two 300 ml portions of 1:1 ammonium hydroxide (in the case of the gels precipitated in the presence of dissolved additive, polymer was also dissolved in this wash solution to the same concentration as used in the starting solutions). The washed precipitate was dried at approximately 130–140°C for 24 hr then calcined at 550–600°C for 3 to 4 hr or until no carbon residue remained.

Addition agents. The polymer addition agents used in the present study were:

1. The polyethylene glycols (CARBO-WAX) and the polyethylene oxides (POLYOX) manufactured by Carbide and Carbon Chemicals Co., New York City, N. Y.

2. The methyl cellulose ethers (METH-OCEL) manufactured by the Dow Chemical Co., Midland, Michigan.

3. The polyvinyl alcohols (GELVA-TOL) manufactured by the Shawinigan Resins Co., Springfield, Massachusetts.

4. The polyacrylamides (PAM, CYANAMER or SUPERFLOC) manufactured by the American Cyanamid Co., New York City, N. Y.

To obtain high concentrations of polymer in the solutions, particularly the high molecular weight species, considerable care had to be taken. If the rate of stirring was too great during the solution process, the tendency for bubble formation was high. The presence of a large amount of trapped air in the gels after the precipitation slowed down the filtration and washing processes and generally reduced the ease of operation and handling. It was found best to melt the polymer, if the molecular weight and type of material allowed, and to add the melt slowly to water at 50–70°C with medium agitation. In the case of samples of polymer of very high molecular

weight the resins were added slowly (over a period of 1 to 3 hr) to cool water with moderate stirring. After the resin was thoroughly dispersed, the temperature was raised slowly to speed the solution process. The tendency for bubble formation was greatest during the heating cycle; hence, agitation at this stage was kept to a minimum.

The Measurement of the Pore Volume Distribution

The pore volume distribution measurements were made by the method of high pressure mercury porosimetry, proposed in principle by Washburn (9) in 1922, developed later by Ritter and Drake (7) in 1945 and verified by Zwietering (10) in 1958. In this technique the amount of mercury that can be forced into a porous solid is measured as a function of the applied pressure. The cosine of the contact angle of mercury with many substances is negative and the surface tension forces therefore oppose the entry of mercury into pores. The surface tension forces can be overcome by the application of external pressure, and the pressure required to press a quantity of mercury into a sample can be used as a measure of the size of the pore that has been penetrated.

The equation relating pressure and pore size is

$$r = (-2S \cos a/P) \times 1.45 \times 10^8$$

where P is the pressure (psia), r is the pore radius (\AA), S is the surface tension of mercury at the temperature of the experiments (480 dynes per cm), and a is the contact angle. For the type of gels investigated here " a " has been shown to be very nearly 140° (7).

A diagram of the dilatometer used to contain the sample is shown in Fig. 1 and simplified diagrams of the low pressure (1–15 psia) and high pressure (15 to 60,000 psia) apparatus are shown in Fig. 2. The pumps, vessels, and electrical connections in the high pressure apparatus were designed and constructed by Autoclave Engineers of Erie, Pa. Very briefly, the procedure used was as follows: The sample to

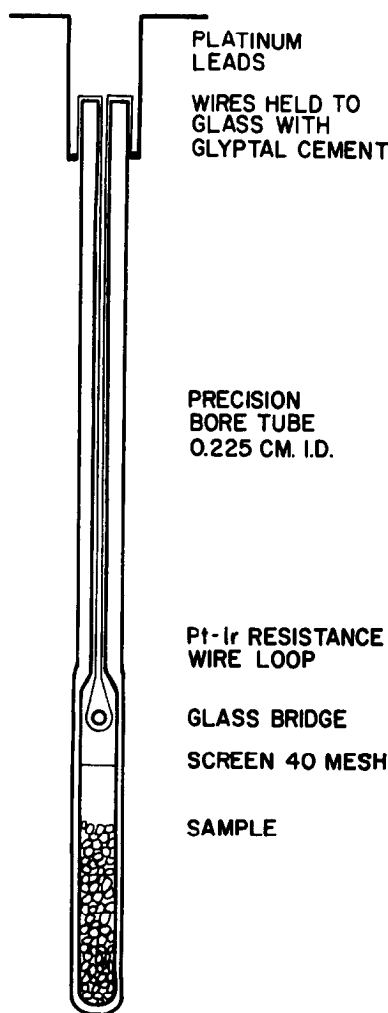


FIG. 1. Diagram of the dilatometer.

be examined ($-14 + 30$ U.S. Standard Screen fraction) was weighed and placed in a dilatometer. The dilatometer was then placed in a very nearly horizontal position in the glass, low pressure apparatus and the sample degassed overnight under vacuum at 200°C . The pressure over the sample after approximately 16 hr evacuation was usually 10^{-3} mm or less. On completion of the degassing operation the dilatometer was filled with mercury at 1 psia. This was done by raising the mercury above the mouth of the dilatometer until the head was equivalent to 1 lb/sq inch. Air was then allowed to bleed slowly into the system through the capillary jet and

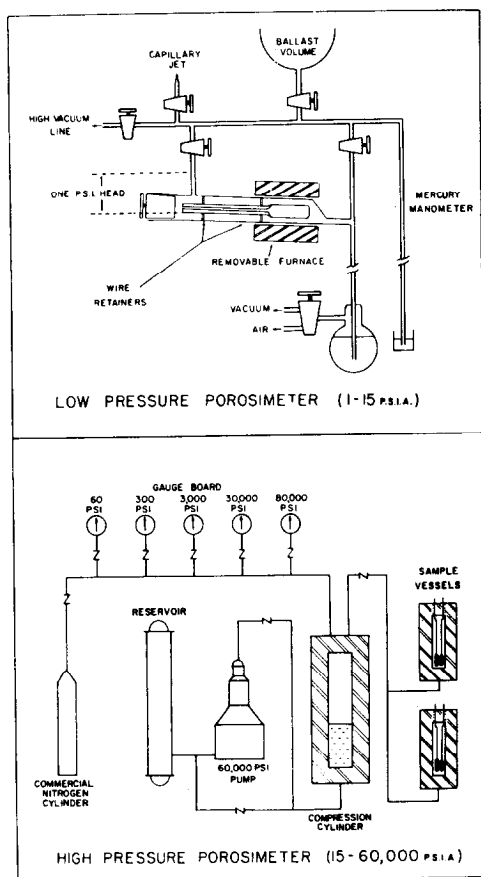


Fig. 2. Diagram of the low and high pressure mercury porosimeters.

the mercury allowed to return to the reservoir until the dilatometer was in view. The air bleed was then shut off and the mercury drawn down into the reservoir with an auxiliary pump. At this point the pressure over the mercury in the dilatometer was very nearly 1 psia (1 psi air pressure plus head of mercury in capillary due to slight slope of the dilatometer).^{*} The pressure

^{*}It was not possible to fill the dilatometers under vacuum conditions because of the inertia of the mercury. The pressure, or head, required to cause the mercury to flow around the granules of sample was governed to a large extent by the particle size. In the experiments reported here the particle size was a -14 to 30 U.S. Standard Screen fraction. A smaller particle size required higher pressures—up to 15-25 psia in certain cases of fine powders.

over the mercury was then increased stepwise up to atmospheric pressure and the volume of mercury forced into the sample measured by noting the change in level in the dilatometer with a cathetometer.

At atmospheric pressure the dilatometer was transferred from the vacuum apparatus to a high pressure vessel. In the high pressure apparatus, gas pressure was applied stepwise from atmospheric pressure up to 60,000 psi. The volume of mercury forced into the sample was measured by following the level of the mercury in the dilatometer by means of the electrical resistance of the fine platinum-iridium wire loop threaded in the capillary. As more mercury was forced into the sample, the level dropped in the precision bore tube exposing more wire and thereby increasing the electrical resistance. The experimental results given in the following sections are presented as *cumulative* pore volume distribution curves, i.e., the total amount of mercury per gram of sample forced into the pore structure is plotted as a function of the applied pressure. In each figure the smallest pore radius penetrated (as calculated from the equation) corresponding to the applied pressure is shown across the top of the plate.

The Measurement of the Surface Area

The total surface area contained in the samples of the gels was measured using the Brunauer, Emmett, and Teller nitrogen adsorption method (11). The apparatus and procedure used were essentially the same as those described by Joyner (12).

The Measurement of the Apparent Bulk Density

The portion of the calcined gels used for the bulk density measurements was the -14 + 30 U.S. Standard Sieve fraction. The sample was poured slowly through a funnel into a weighed 10 ml graduated cylinder. The cylinder plus 10 ml of sample was then weighed, and the weight and apparent bulk density of the powder determined.

The accuracy and reproducibility of the method were affected by any factor, such

as vibration or tamping, that interfered with the packing characteristics of the granules. To reduce the handling and vibration of the graduated cylinder to a minimum, the graduate was cut off and ground square at the 10 ml mark. The excess of granules over the top of the cylinder was removed with a straight-edge, taking care not to shake or tap the cylinder. The funnel used to feed the sample into the graduated cylinder was a standard 50 ml, 60° analytical funnel with a stem length of 1 inch. The funnel was set up such that the tip of the stem was $\frac{1}{2}$ inch above the top of the cylinder. The sample was poured through the funnel as uniformly as possible, usually over a period of approximately 10 seconds.

A DESCRIPTION AND CLASSIFICATION OF THE PORE STRUCTURE OBTAINED USING WATER SOLUBLE ORGANIC POLYMERS

In any discussion of the results of the over-all investigation, a number of classifications are possible depending upon whether interest centers upon the addition agent, the method of preparation, or the effect obtained. In the discussion that follows, the results have been classified into three groups centering on the effect of the addition agent on the pore volume distribution. It is important to appreciate that almost every soluble or dispersible polymer substance has some effect on the porous properties of an inorganic gel. With certain polymers the effects are large, with others the effect is small. The results given here were selected from a large volume of available data in order to indicate the type of control that is possible in the small, intermediate, and large pore size ranges.

Group 1 Additives

Polymers such as the polyethylene glycols (the Carbowax compounds) and the polyethylene oxides (the Polyox resins) bring about a very large increase in the pore volume contained in the pore size range 1000 to 20 Å radius. With only modifications in degree, this effect occurs with all inorganic gels presently in commercial use, such as alumina, silica, and alumina-

silica gels, and with all grades and molecular weights of Carbowax and Polyox. Typical pore volume distribution curves for each type of gel are shown in Figs. 3 and 4.

Alumina-silica gel, approximately 6% SiO₂, prepared without the use of a polymer addition agent, normally has a pore system in the 100 to 20 Å range. The addition of Carbowax 4000 (mol. wt. = 3000-3700) to the hydrous gel in increasing amounts (as shown in Fig. 3) progressively increases the total pore volume and widens the pore size distribution from 100 to 1000 Å. Almost all of the increase in the pore volume brought about by the addition agent occurs as the result of the widening of the pore size distribution. In the gel prepared without additive, the total pore volume was 0.64 ml/g and the pore volume in the region 100 to 20 Å was 0.62 ml/g. The total pore volume prepared with 45% Carbowax 4000 was 2.07 ml/g but the portion which occurred in the 100 to 20 Å range was only 0.72 ml/g. The addition of Carbowax 4000 to silica-alumina gel increases the pore volume in the macropore range without changing the micropore structure appreciably.

Much the same general effect as was obtained with Carbowax in the alumina-silica system occurred also with the pure silica and the pure alumina gels. The broadening effect of Carbowax 20M (mol. wt. = 15,000-20,000) on silica gel is shown in Fig. 3. The direction of the change from the micropore range into the macropore region was the same as occurred in the alumina-silica system. In the case of pure alumina the normal pore size distribution occurred in the region 1000 to 200 Å. The effect of the Carbowax was to extend the pore size distribution from the macropore region into the micropore range. The direction of the change is opposite to that observed with alumina-silica gel and the pure silica gel.

The effect of the molecular weight of the Carbowax compounds on the pore size distribution in pure alumina gel is shown in Fig. 4. The number following the trade name Carbowax corresponds closely to the

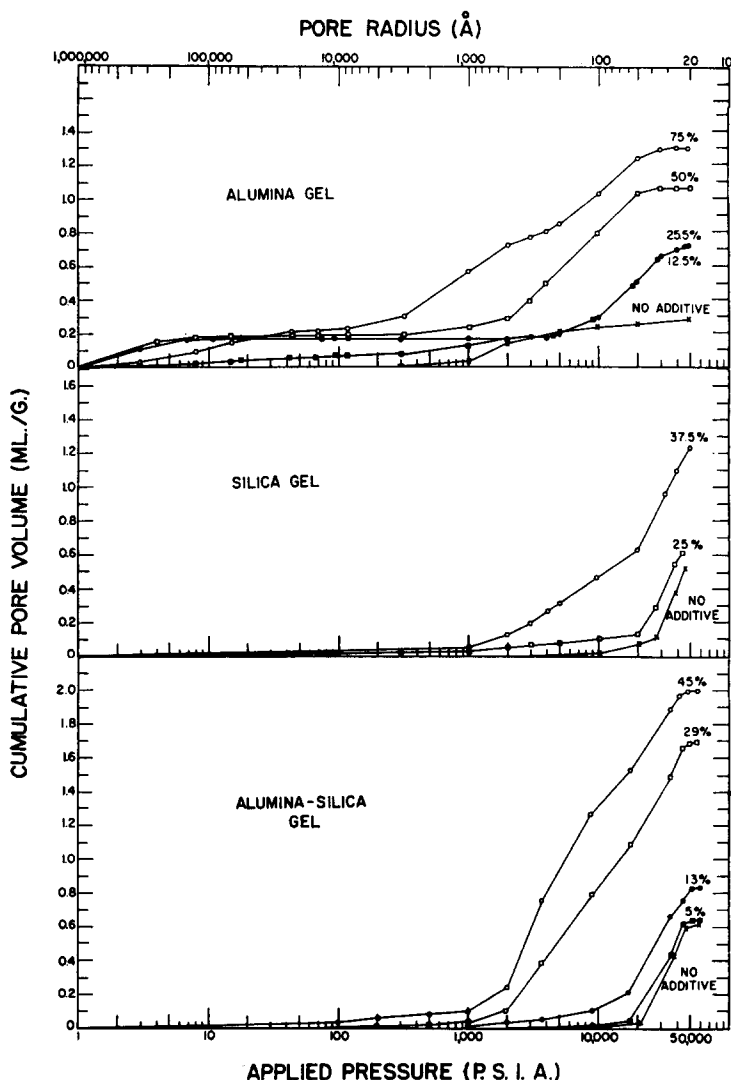


Fig. 3. The effect of polyethylene glycols (Carbowax) on the cumulative pore volume distribution. Alumina and alumina-silica gels: molten Carbowax 4000 blended into the hydrous gel. Silica gels: concentrated solution of Carbowax 20M blended into the hydrous gel.

average molecular weight of the polymer, e.g., Carbowax 4000 is reported by the manufacturers to have an average molecular weight of 3700. The low molecular weight compounds shift the pore size distribution from the region of 1000 to 200 Å completely into the micropore range. The higher molecular weight compounds broaden the pore size distribution in both directions to 10,000 Å and to 200 Å. With the exception of the curve shown in Fig. 4 for Carbowax 20M, the higher the molecu-

lar weight of the Carbowax polymer, the greater the broadening effect on the pore size distribution and the greater the total pore volume.

The effect of increasing molecular weight in the Carbowax series of compounds on the silica and alumina-silica gels is to increase the macropore structure, leaving the micro structure largely unaffected; this follows a similar pattern to that of the concentration curves shown in Fig. 3.

The Polyox resins are very similar in

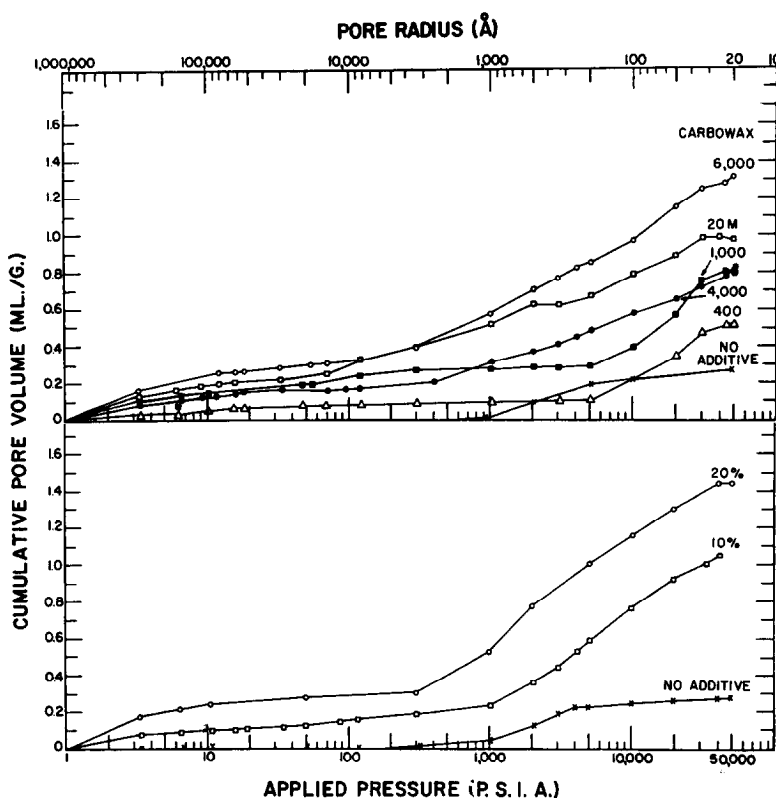


Fig. 4. The effect of molecular weight on the cumulative pore volume distribution in alumina gel. Upper section: 37% by weight Carbowax 400 to 20M blended into the hydrous gel. Lower section: dry Polyox-WSR-35 powder blended into the hydrous gel.

chemical composition to the Carbowax series of additives. The average molecular weight of these polymers is estimated at several hundreds of thousands by the manufacturer. The effect of Polyox on the pore structure of alumina (as shown in Fig. 4) is similar to the effect of the Carbowax compounds. The results with Polyox can probably be regarded as the upper limit of the general effect of increasing the molecular weight of the Carbowax compounds. Unfortunately, because of the limited solubility of the Polyox resins it was not possible to attain a concentration of 37% by weight.

The increase in the pore volume and the changes brought about in the pore size distribution by the Carbowax and the Polyox compounds occur whatever the method of preparing the mixture of the hydrous gel and polymer; i.e., the increase and changes

occur whether the gel is precipitated directly in the presence of the dissolved polymer, or whether the additive is blended into the hydrous gel after its preparation.

The effects of the Carbowax and Polyox additives on the apparent bulk density and surface area of the gels are shown in Table 1. For purposes of comparison, the total pore volume in the samples (as measured by mercury porosimetry) is also shown in Table 1. The changes in the apparent bulk density with concentration are in good agreement with the results of the cumulative pore volume distribution measurements. Large amounts of Carbowax or Polyox decreased the apparent bulk density from 0.66 g/ml to about 0.3 g/ml. The apparent bulk density, as a physical property of the gel, does not reveal a great deal about the pore structure. For a proper

TABLE 1
THE EFFECT OF ADDITIVES ON THE APPARENT BULK DENSITY,
CUMULATIVE PORE VOLUME, AND SURFACE AREA

Gel	Additive	Concentration (% by wt.)	Method of preparation	Apparent bulk density (g/ml)	Cumulative pore volume (ml/g)	Surface area (m ² /g)
<i>Group 1 Additives</i>						
Al ₂ O ₃	No additive	0		0.67	0.28	255
Al ₂ O ₃	Carbowax 4000	12.5	Molten polymer blended into the hydrous gel	0.43	0.72	275
Al ₂ O ₃	Carbowax 4000	25.5		0.44	0.69	265
Al ₂ O ₃	Carbowax 4000	50		0.39	1.06	253
Al ₂ O ₃	Carbowax 4000	75		0.26	1.29	275
Al ₂ O ₃	Carbowax 400	37.5		0.48	0.51	327
Al ₂ O ₃	Carbowax 1000	37.5		0.42	0.79	304
Al ₂ O ₃	Carbowax 4000	37.5		0.39	0.83	259
Al ₂ O ₃	Carbowax 6000	37.5		0.35	1.32	257
Al ₂ O ₃	Carbowax 20M	37.5		0.38	0.97	239
Al ₂ O ₃	Polyox-WSR-35	10	Dry powder blended into the hydrous gel	0.34	1.07	309
Al ₂ O ₃	Polyox-WSR-35	20		0.29	1.44	359
Al ₂ O ₃ -SiO ₂ (6% SiO ₂)	No additive	0		0.480 ^a	0.64	283
Al ₂ O ₃ -SiO ₂ (6% SiO ₂)	Carbowax 4000	5	Molten polymer blended into the hydrous gel	0.388 ^a	0.64	310
Al ₂ O ₃ -SiO ₂ (6% SiO ₂)	Carbowax 4000	13		0.290 ^a	0.83	314
Al ₂ O ₃ -SiO ₂ (6% SiO ₂)	Carbowax 4000	29		0.175 ^a	1.70	338
Al ₂ O ₃ -SiO ₂ (6% SiO ₂)	Carbowax 4000	45		0.154 ^a	2.00	353
SiO ₂	No Additive	0		0.42	0.53	505
SiO ₂	Carbowax 20M	25	Concentrated solution of polymer blended into the hydrous gel	0.20	0.62	—
SiO ₂	Carbowax 20M	37.5		0.18	1.22	266
<i>Group 2 Additives</i>						
Al ₂ O ₃	No additive	0		0.67	0.28	255
Al ₂ O ₃	Methocel-	10	Additive kneaded into the hydrous gel	—	0.84	278
Al ₂ O ₃	USP-400	20		—	1.64	247
Al ₂ O ₃		40		—	1.54	302
SiO ₂	No additive	0		0.49	0.39	279
SiO ₂	Methocel-	5	Additive kneaded into the hydrous gel	0.43	0.60	185
SiO ₂	USP-400	15		0.33	1.05	190
SiO ₂		20		0.27	1.00	295
SiO ₂		40		—	0.71	<50
<i>Group 3 Additives</i>						
Al ₂ O ₃	No additive	0		0.67	0.28	255
Al ₂ O ₃	PAM-75	5	Gel precipitated in the presence of the dissolved additive	0.15	2.07	334
Al ₂ O ₃	PAM-75	10		0.07	5.32	283
Al ₂ O ₃	PAM-75	3.3	Concentrated solution of polymer blended into the hydrous gel	0.59	0.51	278
Al ₂ O ₃	PAM-75	5.0		0.47	0.55	246
Al ₂ O ₃	PAM-75	6.6		0.33	0.99	279
Al ₂ O ₃	PAM-75	8.0		0.33	1.36	299
Al ₂ O ₃	Gelvatol-1-30	10	Gel precipitated in the presence of the dissolved additive	0.19	1.57	324
Al ₂ O ₃	Gelvatol-1-30	15		0.13	2.72	—
Al ₂ O ₃	Gelvatol-1-30	20		0.13	3.96	340
Al ₂ O ₃	Gelvatol-1-30	3	Concentrated solution of polymer blended into the hydrous gel	0.52	0.33	285
Al ₂ O ₃	Gelvatol-1-30	8		0.41	0.81	305

^a Al₂O₃-SiO₂ samples ground to pass 80 mesh screen.

analysis of the system the pore volume distribution measurements are required. Density measurements are, however, easily and quickly obtained, and have been found to be a very useful laboratory control in the preparation of a series of gels with similar additives.

In contrast to the similar effects on the pore volume distribution by all the Group 1 additives, the effects on the surface area of the various gels are very irregular. Each additive and each gel system must be considered separately. With the pure alumina and the alumina-silica gels, the Carbowax compounds bring about a small increase in the surface area. The same additive in the silica gel system causes a marked decrease in the surface area. Unlike the Carbowax compounds, the Polyox resins cause quite an appreciable increase in the surface area of alumina gels. The surface area of an alumina gel prepared without an additive was 255 m²/g. The addition of Polyox increased the surface area up to 350–360 m²/g. The increases observed with the Polyox resins follow the same general trend with concentration as do the effects on the pore volume and the apparent bulk density.

Group 2 Additives

The second class of behavior is shown by the Methocel series of compounds (of which Methocel-USP-400 is typical) with alumina and silica gels in Fig. 5. With the Group 1 additives the greater part of the change in the pore volume distribution occurred in the small and intermediate pore size ranges. The increase in the pore volume brought about by the Methocel compounds, on the other hand, occurred generally as the result of the creation of a large macropore system. When present in sufficiently high concentrations (40% by weight) Methocel USP 400 prevents entirely the formation of the pore structure characteristic of the normal gel made without additive, substituting in its place a large macropore system. At intermediate concentrations, proportionate combinations of large and "normal" pore sizes occur.

The effect of the Methocel series of

additives on the apparent bulk density and surface area is shown in the center section of Table 1. In the case of the Methocel series of additives the apparent bulk density cannot always be regarded as a guide to the pore volume. At the high concentrations of additives the gels formed are friable and the test specimens for the bulk density measurements frequently broke up on handling. The net result was that the apparent bulk density measurements are higher than they should be because of the presence of fine particles. For silica gel it was found that the bulk density measurements were useful as a laboratory control up to approximately 20% by weight of Methocel. At higher concentrations than 20% density results do not give a reliable measure of total pore volume in the gel.

The effect of the Methocel additives on the surface area of the gels is marginal. A large amount of additive increases the surface area slightly, whereas a small amount has an immeasurable effect. Extreme concentrations (40%) of Methocel increase the surface area of alumina gel slightly, but cause a marked decrease in the surface area of silica gel (silica gel is easily sintered and the decrease in surface area here is probably due to poor temperature control in the process of burning off the large amount of organic matter).

In general, the mixture of hydrous oxide gel and Methocel cannot be made by dissolving the additive in the solutions used to prepare the gel. The reasons for this are twofold. First, the solubility of Methocel in water is very limited. A practical working solution is 2 to 3% by weight. Even at this concentration the solutions are very viscous and difficult to manipulate. Second, in the cases where aluminum salts are present in the solutions, any Methocel added to the system is salted out. In the examples shown in Fig. 5, the powdered Methocel was blended or kneaded into the hydrous gels after they were formed.

Group 3 Additives

The third type of effect on the pore size distribution is illustrated by the polyacrylamide (PAM) and the polyvinyl alcohol

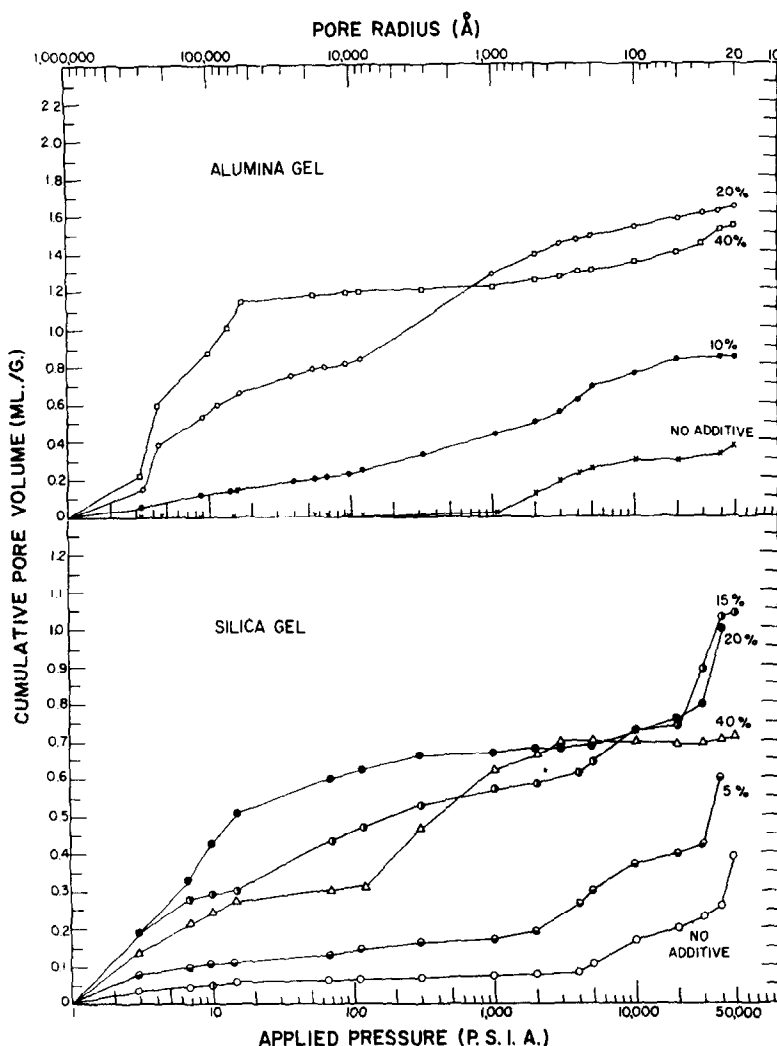


FIG. 5. The effect of methyl cellulose (Methocel-USP-400) on the cumulative pore volume distribution. Dry powder kneaded into the hydrous gel.

(Gelvatol) polymers. Typical pore volume distribution curves obtained with alumina gels prepared using these polymers are shown in Figs. 6 and 7. These additives extend the pore size distribution in alumina in both directions (from the normal pore size distribution in alumina prepared without additive) to 100,000 Å and to 50 Å, with a tremendous increase in the total pore volume of the gel. The largest pore volume obtained to date is 5.4 ml/g in an alumina gel prepared by precipitating hydrous aluminum hydroxide from a solution containing 10% PAM-75.

With both of these additives, PAM and

Gelvatol, the effects are greatest when the additive is dissolved in the solutions used to prepare the gel; i.e., the mixture of gel and polymer is prepared by precipitating the gel from a solution containing the dissolved polymer. To a degree the changes in the pore size distribution also occur when the additive is blended into the hydrous gel, as shown in the upper sections of Figs. 6 and 7. An important point to notice here is that the amount of PAM or Gelvatol additive required to open up the pore structure of alumina is considerably less than the amount of Carbowax additive. The effect of 8% PAM-75 (added to the

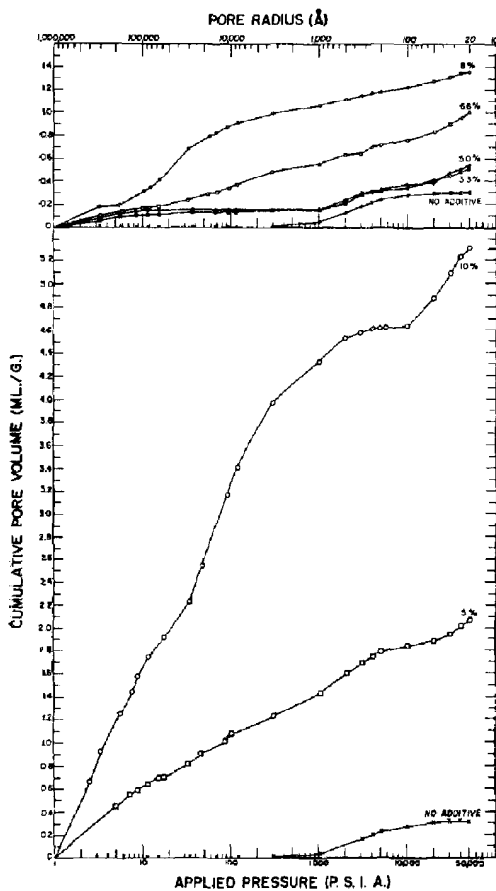


FIG. 6. The effect of polyacrylamides (PAM-75) on the cumulative pore volume distribution in alumina gel. Upper section: concentrated solution of PAM blended into the hydrous gel. Lower section: gel precipitated in the presence of dissolved PAM.

hydrous gel after the precipitation step) on the over-all pore volume in alumina is approximately equal to the effect of 75% Carbowax 4000. The pore range effected by each additive is different, however. PAM-75 brings about a significant increase in the pore volume contained in the pore range 100,000 to 50 Å, while the effect of Carbowax 4000 is restricted to the 1000 to 50 Å range.

The effects of the polyacrylamide and polyvinyl series of polymers on the apparent bulk density and surface area are shown in the last section of Table 1. A very large decrease in the apparent bulk density

of alumina gel occurs with both types of polymers when the gel is precipitated in the presence of the dissolved additive. Approximately 15% Gelvitol or 5% PAM lowers the bulk density from 0.67 g/ml to nearly 0.1 g/ml. In the course of handling these particular samples it was observed that they were less friable than the gels made with the Methocel additives, even though the bulk density was less.

The surface areas of the alumina gels prepared with the PAM and Gelvitol polymers are also appreciably greater than the gels made without additive. Five to ten per cent of either additive increases the surface area from 255 m²/g to approximately 300 m²/g. The effect is not as great as in the case of the Polyox additive, however, where surface areas as great as 350 m²/g were observed.

METHODS OF MODIFYING THE PORE STRUCTURE OF GELS PREPARED WITH ADDITIVES

All of the cumulative pore volume curves shown above were obtained with granular specimens made by lightly grinding the pieces of gel as they came out of the calcining furnace. Each type of distribution can be further modified by the use of the proper pelleting technique. Most of the pore volume distribution curves obtained with the granular gels extend over quite wide ranges, say 10⁷ to 10⁴ Å radius or 10⁴ to 10³ Å radius. By proper pelleting, a granular or powdered gel with a wide pore distribution in one range can be made into a pellet with a much more narrow pore radius distribution in the next lower range. For example, a gel made with polyvinyl alcohol (Gelvitol) or polyacrylamide (PAM) in the granular form has a wide pore system in the very large pore region. By grinding this type of gel lightly and pelleting at a low pressure, pellets can be made containing a relatively narrow pore volume distribution in the region of 1000 Å radius. Of course, it must be appreciated that the process of grinding and pelleting greatly reduces the total pore volume of these gels. In the granular form, gels made with PAM or Gelvitol have total pore

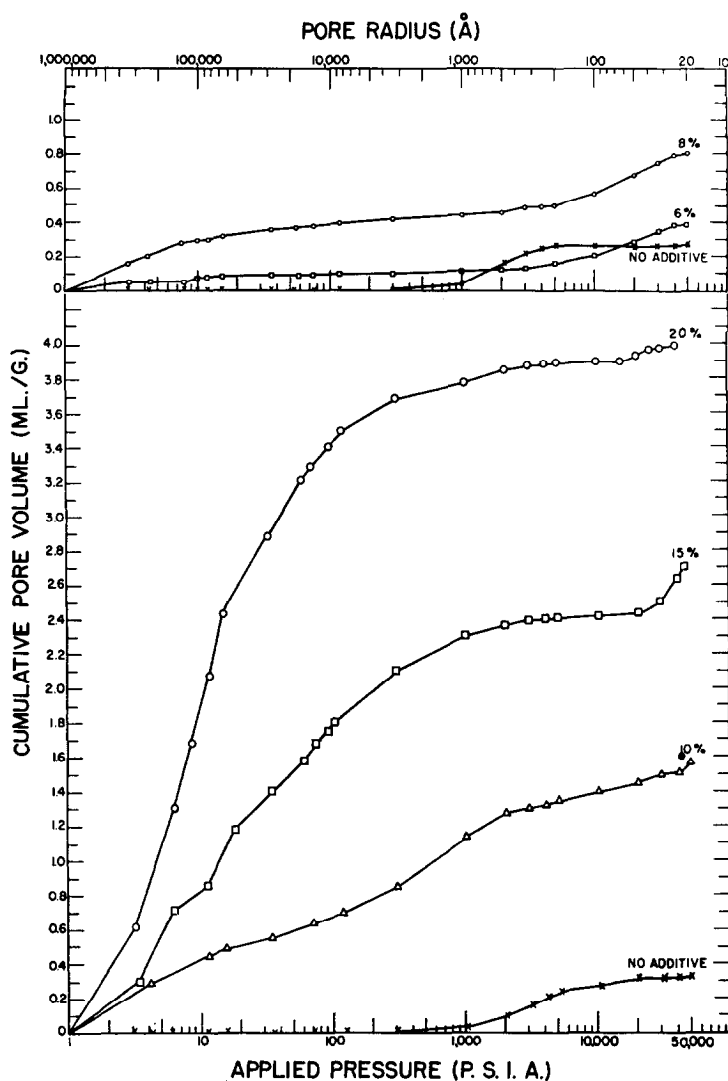


Fig. 7. The effect of polyvinyl alcohols (Gelvatol-1-30) on the cumulative pore volume distribution in alumina gel. Upper section: concentrated solution of Gelvatol blended into the hydrous gel. Lower section: gel precipitated in the presence of dissolved Gelvatol.

volumes in the region of 4 to 5 ml/g. In the pelleted form the total pore volume is approximately 0.6 to 1 ml/g.

Although conventional pelleting apparatus operating on a constant volume basis is adequate for many purposes, it has been found that a much superior technique is to pellet at a constant pressure. Slight variations in the rate of feed of the powdered gel in a constant volume punch and die assembly can change the actual pelleting pressure and hence the pore volume distri-

bution to a great extent. For the present study a conventional pellet press was modified so that the lower die was supported against a hydraulic ram maintained at a predesignated pressure. In the pelleting process, when the desired pellet pressure is attained, the die and ram slip against a constant pressure hydraulic "cushion" so that the pellet is ejected without any portion being subjected to a greater pressure than the predesignated value. A complete description of the pellet press, the method

of operation, and the effect of pressure, particle size, binders, etc., on the final pore structure of conventional and highly porous gels is in the course of preparation.

Another way of modifying the effect of one addition agent on the pore structure of a gel is to add a second addition agent. An indication of the effects that can be obtained by selecting various combinations of additives is shown in Fig. 8. In general,

performing a very simple graphical differentiation on such plots the pore size distribution (dv/dr vs. r) contained in the gel can be determined. Typical pore size distributions in alumina gels made with polyacrylamides and polyethylene glycols are shown in Fig. 9. The corresponding cumulative pore volume distributions are shown in Figs. 3 and 6. Very little additional information can be obtained from

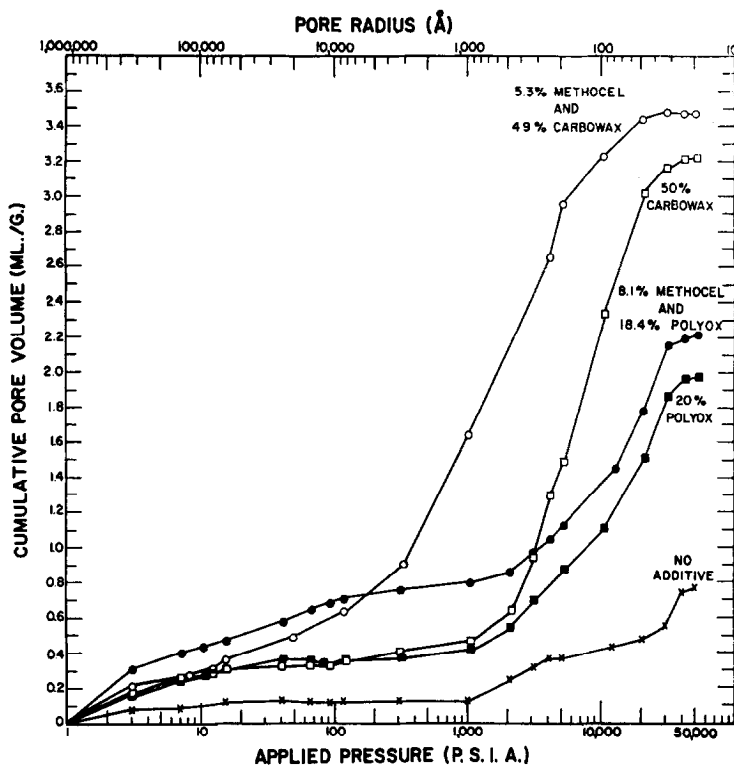


FIG. 8. The effect of combination of additives on the pore volume distribution in alumina gel. (Molten and powdered additives blended into hydrous aluminum hydroxide gel manufactured by the Reheis Company of Berkeley Heights, New Jersey.)

the addition of Methocel to either Carbowax or Polyox mixtures has the effect of broadening the pore size distribution obtained with either separately. The principal effects of each of the additives alone has already been described.

DISCUSSION

The results of the pore volume measurements have all been presented as "cumulative" pore volume distribution curves. By

the pore size distribution than from the cumulative plot, but it is of interest to note that both types of polymer result in roughly linear ($\log \times \log$) distribution curves over a thousandfold change in pore radius. Pore size distribution calculations also show maxima in certain pore size ranges (such as the case of the alumina prepared with 25% Carbowax 4000) that are not immediately obvious from the semilogarithmic cumulative plots. For a

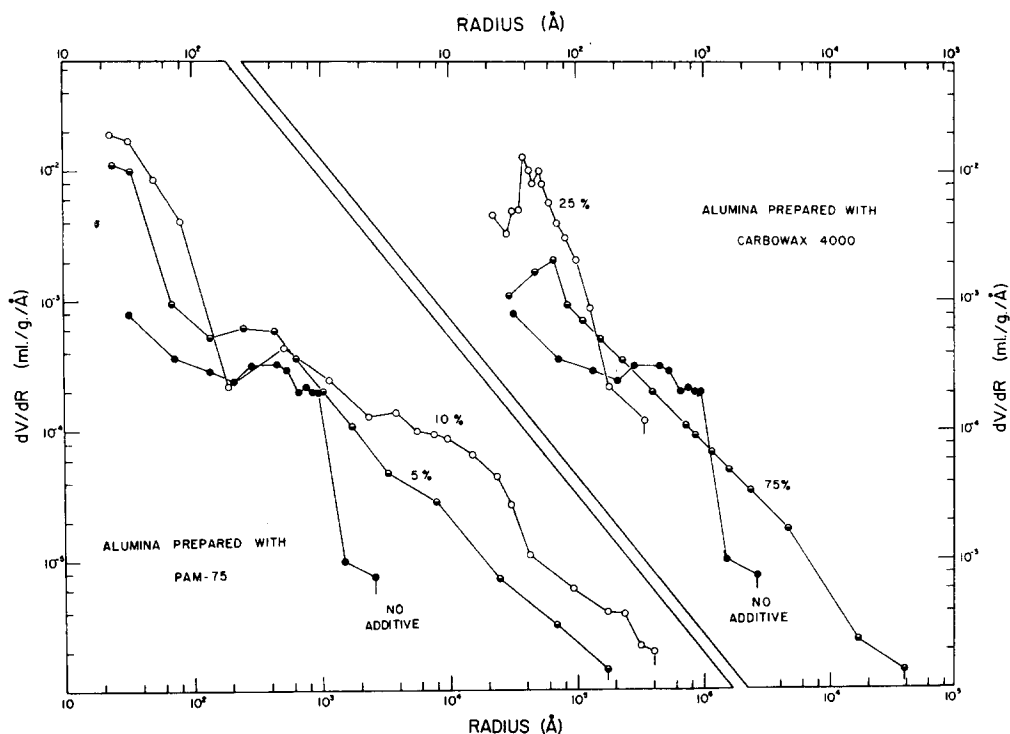


FIG. 9. The effect of additives on the pore size distribution in alumina gel. Left section: gels precipitated in the presence of dissolved PAM-75. Right section: molten Carbowax-4000 blended into the hydrous gel.

more complete appreciation of the pore structure, both types of distribution plots are really required.

Almost every procedure for the preparation of a calcined gel with a large internal surface area and pore volume can be divided into two parts: 1. the preparation or precipitation of the hydrous form of the gel, and 2. the drying or dehydration process. From the point of view of the porous nature of the gel the dehydration process is usually regarded as the most important. In the course of drying the hydrous gel shrinks in volume many fold. This shrinkage is attributed to the high surface tension of the water contained in the gel (13). The thin skeletal structure of the gel is believed to be drawn together by the surface tension forces as the water content is gradually reduced by heating and evaporation. Eventually, there is a point in the dehydration and shrinkage processes where the skeletal walls become strong enough to withstand the surface tension and other interfacial

forces and the remainder of the water can be removed with very little additional change in the structure.

A large part of our investigations centered around the possible effect of our additives on the surface tension of the water contained in the hydrous gel and its effect on the drying process. In one series of experiments samples of alumina gel were made using various surfactants as additives, and in another the effect of polymers such as the polyethylene oxides and the polyvinyl alcohols on the surface tension of water was determined. In general additives such as the Carbowax and Gelvatol polymers have only a small effect on the surface tension by comparison with surfactants. Moreover, surfactants used as additives in the manner described in this report have little effect on the pore structure. It was concluded, therefore, that the surface tension is not the principal cause of the changes in the present circumstances.

There are three outstanding points to be

taken into account in the postulation of a mechanism for the action of the various groups of additives. First, in order to produce an appreciable effect on the pore structure the polymer must be water soluble (or dispersible) in *large* concentration. This requirement alone seems to exclude indirect modes of action such as through the modification of the surface tension or through the formation of thin films, etc. Second, certain of the polymer additives possess reactive functional groups capable of forming chemical bonds with metal cations; these are much more effective in altering the pore structure when dissolved in the solutions before the precipitation of the gel. Third, those polymers that do not possess reactive functional side groups are equally effective whether the mixture of additive and gel is prepared by the coprecipitation technique or by blending the additive into the hydrous gel after the precipitation process. It is the presence or absence of the functional side groups that is felt to be important in determining whether the effect on the pore structure arises simply through changes in the drying process or whether the effect is due to changes in the nature of the hydrous gel with consequent changes in the mechanism of dehydration.

Stated in general terms, it is our belief that the polymer additives act to change the pore structure in two ways depending upon whether or not the polymers possess reactive functional groups for the metal cations in question. In the first class, the reactive polymers, are the polyacrylamides and the polyvinyl alcohols—the Group 3 additives. In the second class, the nonreactive polymers, are the polyethylene glycols, the polyethylene oxides and the methyl cellulose ethers, i.e., the Methocel compounds—the Group 1 and Group 2 additives. The Methocel compounds, the Group 2 additives, are regarded as a special case of the nonreactive additives as will be explained more fully later.

For the nonreactive group it seems likely that the same mechanism of pore formation applies as in the case of normal or “no

additive” gel; the function of the polymer is simply to prevent the collapse of the gel structure under the surface tension and other interfacial forces involved in the dehydration process. The Carbowax and Polyox compounds are relatively stable in air up to 250°C. In the early stages of the drying and calcining processes the adsorbed and occluded molecules or colloidal particles of the polymers probably act as “separators” in the gel network, up to the temperature required to set the gel. Above the flash point of the Carbowax the supporting agent will oxidize out leaving the pure calcined gel. As mentioned before, this view of the mechanism for the nonreactive group of polymers is supported by the fact that the effects occur whether the mixture of gel and polymer is prepared by coprecipitation techniques or whether the polymer is blended into the hydrous gel after it has precipitated.

In the case of the derivatives of methyl cellulose, the Methocel additives (Fig. 5), increasing amounts of this additive increase the pore volume by creating very large pores in the micron range. At the highest concentrations the pore structure, characteristic of the normal gel, is not present. This in itself is a striking exception—usually the changes in the pore structure are always in addition to the conventional gel structure. Aqueous solutions of Methocel differ from almost all other types of polymer solutions inasmuch as they set to a rigid gel on heating. It would seem that, when a mixture of inorganic gel and Methocel is heated in the drying process, if sufficient Methocel is present, the system sets and the inorganic matter is forced to dry to the conformation of the Methocel gel structure. It is believed to be a case of relative strengths where, under certain circumstances, the Methocel structure is the stronger. At low and intermediate concentrations of Methocel the mechanism is probably a combination of this process and the bulking agent effect proposed for the polyethylene glycol and oxides.

The tremendous changes in the pore structure brought about by the reactive

group of additives—those additives which possess reactive side groups, the polyacrylamides and polyvinyl alcohols—suggest that these compounds radically modify both the hydrous gel structure and the dehydration processes. The belief that the hydrous gel structure itself is modified is supported by the fact that the additive is most effective when dissolved in the solutions prior to the formation of the gel. The gel probably surrounds the polymer molecule or particle with a coordinate layer. Subject to shrinkage, gasification, and other changes in the calcination process, the final pore volume distribution would correspond to the volume occupied by the polymer. A variation on this mechanism would be the case where an aluminum compound is formed with the polymers. Work is continuing on this point.

The changes in the pore structure brought about by the PAM and Gelvatol polymers added after the precipitation process, i.e., to the hydrous gel, are probably the result of a combination of both mechanisms, the supporting agent action proposed for the polyethylene glycols and the complex compound formation postulated for the polymers possessing reactive side groups.

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