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MICROSPHERE FORMING CONDITIONS FOR ThO_2-UO_3, ThO_2 AND UO_2 SOLS: FURTHER FACTORIAL EXPERIMENTS

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ABSTRACT

A four-variable factorial experiment in forming sol-gel microspheres in a 2-ethyl-1-hexanol (2EH) fluidized column was made, using three types of ThO_2-UO_3 sols, one ThO_2 sol, and one UO_2 sol. The ThO_2-UO_3 sols had been prepared by solvent extraction, the ThO_2 sol by steam denitration, and the UO_2 sol by the CUSP (Concentrated Urania Sol Preparation) process. The concentrations of the surfactants (Ethomeen S/15 and Span 80), the water, and the nitric acid in the 2EH were varied. The sensitivities of the sols to column conditions were found to be as follows: ThO_2-UO_3 > UO_2 >> ThO_2.

The recommended column conditions for the ThO_2-UO_3 sols are as follows: a low Ethomeen S/15 concentration (about 0.05%), complete exclusion of Span 80 to avoid pitting, a water concentration of 0.5 to 1.7 vol %, and a pH range of about 3 to 4. Wider tolerances are possible for steam-denitrated ThO_2; only one set of conditions is to be completely avoided (a pH about 0.8, a water concentration as low as about 0.5 vol %, and low surfactant concentrations of 0 to 0.05%). The data for the UO_2 sol, although incomplete, indicate the need for the addition of Span 80 to the 2EH to prevent clustering. Good results were obtained with blends of Span 80 and Ethomeen S/15. Statistical evaluation showed both primary and secondary effects for the ThO_2-UO_3 sols.

1. INTRODUCTION

This paper reports the continuation of a sol-gel microsphere formation factorial experiment that was described previously.[1-3] The earlier experiment can be briefly summarized as follows. A laboratory study was made to determine the effects of three variables in the formation of 75% ThO_2 - 25% UO_3 gel microspheres in 2-ethyl-1-hexanol (2EH) columns. These variables were water content (0.4 vs 1.6 vol %), surfactant concentration (0.05 vs 0.50 vol %), and acid concentration (0.001 vs 0.01 $\underline{M}$ HNO_3) of the 2EH. Only one surfactant,

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Ethomeen S/15, was used in order to hold the number of variables to a minimum. For these sols, Ethomeen was felt to be of more importance than Span 80, the other commonly used surfactant. Results were evaluated by visual inspection of the gel microspheres and by statistical methods commonly used in factorial experiments. The statistical evaluation was complicated by the fact that the error distribution turned out to be bimodal. It was evident, however, that conditions favoring the highest yields of round microspheres tended toward the use of low surfactant levels rather than high levels, and that two cross effects were influential. These cross effects tended to produce improved yields when the acid and Ethomeen S/15 concentrations were balanced (either both high or both low), and the water and Ethomeen S/15 concentrations were not both high or both low. The following conditions were found to be best for forming microspheres: 0.05 vol % Ethomeen S/15, 0.001 M HNO_3, and 1.6% H_2O in the 2EH. Photomicrographs of spheres made from three of the ThO_2/UO_3 sols illustrated the findings.

The data presented in this report present a continuation of the study discussed above, through the addition of Span 80 at 0.05 and 0.50 vol % levels, to the eight solvents previously used (or to their equivalents). Two of the ThO_2-UO_3 sols (1-A and D) were used in the earlier work; one (sol G) was different. A steam-denitrated thoria sol and a UO_2 sol were added to provide supplementary information relating to these sol types.

2. DESIGN OF THE EXPERIMENT

The design of the experiment (Table 1) was similar to that used in the previous study,[1] with the exception of the changes noted below.

2.1 Composition of the Solvents

At the beginning of this experiment, the water contents of the eight solvents (Table 1) were higher, by 0.1 vol %, than in the previous experiment (i.e., 0.5 and 1.7 vol % vs 0.4 and 1.6 vol %). Some of the solvents had been used in the previous experiment and hence had absorbed water during microsphere preparation, while the others were freshly prepared to contain the increased water content. In the present experiment, each solvent was first used for preparing microspheres without the addition of Span 80 (i.e., at the zero Span level; see Table 1, variable 4); then sufficient Span 80 was added to give a 0.05% concentration and the microsphere formation runs were repeated. Finally, after further addition of Span 80, each solvent was tested at the 0.5% Span 80 level. Thus 24 different solvent compositions were evaluated.

2.2 Sols

Five sols were used in this experiment (Table 2). Two of the 75% ThO_2 - 25% UO_3 sols (A and D), which had been used previously represented cocurrent-solvent-extracted material prepared with and without a digestion step. Sol G was a countercurrent-solvent-extracted material having a lower NO_3^-/metal mole ratio (0.07 vs 0.12), a lower concentration (1.2 vs 2 M), and a higher Th/U atom ratio (4.25 vs 3.0). Sol GS-26 was a steam-denitrated thoria product containing no uranium, while CUSP-7 was a urania sol prepared by the CUSP process.[4,5]

2.3 Columns and Column Operators

A single operator (A. B. Meservey) used the same microsphere forming column (B-13) to prepare all of the microsphere products described in this report. (In the previous experiment, two columns and two operators were used.) Thus the present results contain biases common to one column and one operator only. However, the net effect is to make comparisons among the sols and solvents more internally consistent, since possible column and operator differences have been eliminated.

3. EXPERIMENTAL

The procedure used in the experiment reported here was essentially the same as that used in the earlier work;[1] only minor changes were made. In every case, 0.25 ml of the desired sol was dispersed in a small column into 1 liter of a given solvent. Since no still for water removal was employed, the water content of each of the solvents had increased to about 0.6% and 1.8% at the end of the 0.05% Span 80 series, and to about 0.7% and 1.9% when the 0.5% Span 80 series was complete. (We assumed that 0.20 ml of water was absorbed into the solvent per sol sample.) When fresh solvents were made, their water contents were adjusted initially to 0.5% and 1.7%. The ThO_2 (white) and UO_2 (black) sols were fluidized in the column at the same time as one of the ThO_2-UO_3 sols (red) since the colors of the products permitted easy identification when examined under the microscope. The gel microspheres were dried in air at about 50°C as previously described,[1] and their quality was evaluated in terms of amount (%) and overall severity (0-10 scale) of defects.

4. RESULTS AND DISCUSSION

Several results were clearly obvious on examination of the microspheres, and can be seen in the photomicrographs shown in Figs. 1-8. These results are discussed at length under the headings that follow; they are summarized in Table 3.

4.1 Differences Among Types of Sols

Comparisons of the various sols used in the study reported here showed that the ThO_2-UO_3 sols were quite sensitive to column conditions, since the microspheres formed from them tended to break or show evidence of deformation; however, they had no apparent tendency to cluster. Microspheres formed from the UO_2 sol resisted deformation much more readily, but were prone to cluster. Extensive cracking occurred in the UO_2 microspheres on exposure to air, due to oxidation. Product from the ThO_2 sol was very resistant to deformation and breakage, except under extreme conditions (described in a later section); there were almost no problems due to clustering.

4.2 Differences Among the ThO_2-UO_3 Sols

Sol A (Table 2), which had been prepared without the digestion step, was the most sensitive with respect to cracking and deformation of product. Sol D, which was similar to sol A, except that it had been subjected to a

2-hr digestion during preparation in order to improve crystallinity, was less sensitive. Sol G, which had also been prepared by using the digestion step, was much superior to sols A and D; however, since it had three other variations in makeup (lower nitrate content, higher ThO_2/UO_3 mole ratio, and lower molarity), we are unable to say, without further testing, whether any single factor caused the superiority.

4.3 Effects of Span 80 When Used in Combination with Ethomeen S/15

Span 80 is a strong promoter of pits in ThO_2-UO_3 microspheres, the depth of the pits increasing with increasing acid concentration. An increase in Ethomeen S/15 concentration decreases this pitting effect. Span 80 decreased the amount of clustering in the UO_2 microspheres, and also in the ThO_2 microspheres when it occurred (solvent 6). In the case of the ThO_2 sol, the presence of Span 80 halted a cracking effect, which occurred at low Ethomeen S/15, low water, and high acid concentrations. Slight pitting of ThO_2 microspheres occurred at 0.5% Span and low water concentrations when the Ethomeen S/15 concentration was low, but not when the Ethomeen concentration was high. This again demonstrates that Ethomeen helps to protect microspheres from Span-caused pits, possibly by means of a softening effect on a shell or skin which may form during dehydration.

4.4 Effects of Water and Acid Concentration Levels

Although cross effects become too complex to be visually obvious in every case, a few water and acid effects are quite prominent in the photomicrographs (Figs. 1-8) and in the data in Table 3.

The most noticeable effects of the water content of the column solvent are found at low Ethomeen— high acid concentrations (Fig. 5 vs Fig. 6). The ThO_2-UO_3 microspheres that were formed in 2EH having a high concentration of water but containing no Span 80 are granular; those formed in 2EH with low water contents are cherry-pitted and vitreous. With Span 80 present, "raisin" deformations occurred in microspheres formed from sols D and G in 2EH containing 1.7 vol % H_2O;

crush-pitting was evident at the lower water concentration (0.5%). Slower drying of the microspheres formed in solvent with the higher water content evidently alters the nature of the outer skin, causing it to wrinkle (raisin), while faster drying promotes cherry-pitting. Solvent 6, which has a low water content, caused complete breakage of pure thoria sol microspheres in the absence of Span 80; this effect was diminished when enough Span 80 was added to the solvent to give a final concentration of 0.05%, and was entirely eliminated by using a Span concentration of 0.5%. No breakup of pure thoria was observed in solvent 5, with 1.7% H_2O.

The acid effect is easily seen in all four solvent pairs (7 vs 5, 3 vs 1, 8 vs 6, and 4 vs 2). The Span-containing solvents had a greatly increased pitting effect on the ThO_2-UO_3 microspheres at the higher acid levels. Breakup of the ThO_2 microspheres occurred only at the high acid concentration level (solvent 8 vs solvent 6), and granularity of the ThO_2-UO_3 microspheres occurred only at the high acid - high water - low Ethomeen concentrations when Span was absent (solvent 7 vs solvent 5).

4.5 Detailed Study of the Photomicrographs

Comparisons of the 72 photomicrographs shown in Figs. 1-8, representing solvents 1-8 respectively, can become confusing if not followed in a routine sequence. Many sequences are possible, and several different orders yield more information than any one sequence alone. One convenient way of grouping is on the basis of water content, looking first at all the results with high water contents (Figs. 7, 5, 3, 1) and then at the results for low water contents (Figs. 8, 6, 4, 2). Within each group of four figures, we can readily compare the results of low and high Ethomeen S/15 concentrations. Also, at each Ethomeen concentration, the effects of a low and a high acid concentration can be seen. Each of the figures shows the effects of three Span 80 concentrations (increasing from left to right in the figures, and designated a, b, and c in Table 3) and the three ThO_2-UO_3 sols (top to bottom). A few ThO_2 and UO_2 microspheres are included, usually with the product from sol A, and in two cases with the product from sol D.

4.5.1 Figure 7 (Solvent 7)

The superiority of sol G over D, and of D over A, which is evident in this figure, will be a dominant theme throughout the entire group of figures. Often, comparisons can be most readily made, as in this case, by observing the depth of pitting as the Span 80 concentration is increased. The devastating effect of Span on the ThO_2-UO_3 microspheres is clearly seen, both from the incidence and depth of pits in the photomicrographs, and the decreasing yields with increasing Span 80 listed in Table 3. Several good-quality ThO_2 and UO_2 microspheres are included with the microspheres formed from sol A in 2EH containing 0.05% and 0.5% Span. Photomicrographs of ThO_2 and UO_2 microspheres formed in the absence of Span 80 are not available except for the ThO_2 product that is shown with sol D product in Fig. 6. (However, yields and characteristics at all levels are given in Table 3.) Note that 100% yields are possible from sols D and G under the conditions of solvent 7 when no Span is present.

4.5.2 Figure 5 (Solvent 5)

Comparison of Fig. 5 with Fig. 7 reveals the effect of the pH of the column solvent on the microspheres prepared from ThO_2-UO_3 sols. In the presence of Span 80, the deformation is much more severe at the lower pH than at the higher pH, apparently because of earlier hardening of the skins of the drying microspheres. Subsequent outward migration of water causes the skin to collapse more generally than is the case when droplet shrinkage has progressed further prior to skin hardening. In the absence of Span, there is a granulation effect on products formed from sols A and D, as discussed previously. However, the deformation and breakup of microspheres formed from sol G in column solvent containing no Span 80 are not expected, and seem to indicate either contamination of the solvent with Span 80 or a mixup of samples. The ThO_2 microspheres were not deformed in solvent 5. No UO_2 microspheres were formed in this solvent.

4.5.3 Figure 3 (Solvent 3)

Comparison of Fig. 3 with Fig. 7 shows the effect of high Ethomeen S/15 concentration in the solvent; however, solvent 3 also has a considerably higher pH than the solvent represented by Fig. 7. Figure 3 shows cracking and pitting from high Ethomeen concentrations in the absence of Span; these defects were considerably reduced for sol G (but not for sols A or D) by the addition of Span. Span-caused "wrinkle pits" at low Ethomeen concentration (Fig. 7) have been replaced in Fig. 3 by cherry pits and breakage in products of sols A and D, and by smooth, unbroken surfaces in product from sol G. Evidently, the surfaces were not hardened as early by Span 80 when the Ethomeen S/15 and pH were at higher levels.

4.5.4 Figure 1 (Solvent 1)

The low pH version of solvent 3 (i.e., solvent 1, Fig. 1) also shows the beneficial effect of a high Ethomeen S/15 concentration in the presence of Span 80. At 0.05% Span, the quality of the products appears to be much higher than when the Ethomeen concentration is low (Fig. 5). At 0.5% Span, the beneficial effect is reduced, but is still present, because of the low pH (compare with Figs. 3 and 7).

Figures 1, 3, 5, and 7 show the results of using solvents having a water content of 1.7%. Figures 2, 4, 6, and 8 show effects at the 0.5% level. In general, the lower water level led to faster drying and earlier hardening of the microsphere surfaces, and accentuated the effects of Span 80.

4.5.5 Figure 8 (Solvent 8)

Figure 8 shows excellent results in the absence of Span 80, similar to those of Fig. 7, indicating a high tolerance of ThO_2-UO_3 sols for a wide range of water concentrations in the solvent when the Ethomeen concentration is low and the pH is 3.7 to 3.8. Span-caused pitting under the conditions represented by this solvent does not differ greatly from that observed at the higher water concentration (Fig. 7). Shallow pits are present in the ThO_2 spheres at both water levels at a Span 80 concentration of 0.5%; however, such pits are absent at the higher Ethomeen S/15 concentration level (See Figs. 3 and 4).

4.5.6 Figure 6 (Solvent 6)

Decreasing the pH from about 3.7 to about 1 intensifies the pitting effect of Span 80 (compare Fig. 6 with Fig. 8). The skins hardened earlier in solvent 6, which is drier than the solvent represented in Fig. 5, so that the pits are more localized. In the absence of Span, the granularity characteristic of product formed in solvents with high water contents (Fig. 5) has been replaced by a vitreous state, with cherry pits (Fig. 6). The ThO_2 microspheres in this low Ethomeen solvent tended to shatter in the absence of Span (with sol D), and showed definite cracking when a low level of Span was used (with sol A); however, they remained intact at a Span concentration of 0.5%. This anti-cracking effect of Span on thoria is an important finding. The "roly-poly" shapes of the sol G microsphers at 0.5% Span, with the deep holes that resemble blowout craters, are unique. Close examination showed the holes to be wrinkle-pits from inward shrinkage, like the others. The UO_2 sol was not used to form microspheres with solvents 5 and 6.

4.5.7 Figure 4 (Solvent 4)

An obvious effect of a high Ethomeen S/15 content in the solvent is to decrease the pitting caused by the presence of Span 80 (Fig. 4 vs Fig. 8); this has also been demonstrated with solvents having high water contents (Fig. 3 vs Fig. 7). High yields of product thus become possible in the presence of Span when sols typical of sol G are used. Slight cracking in the thoria product (see Table 3, solvent 4) was not improved by the addition of Span 80; however, this seems to be a different type of cracking than that decreased by the presence of Span 80 in solvent 6 (Fig. 6). Whereas the ThO_2 microspheres shattered into small bits in solvent 6, they broke into large pieces in solvent 4.

4.5.8 Figure 2 (Solvent 2)

Figure 2, the low pH version of Fig. 4, again shows the increase of Span-pitting when a solvent with a low pH is used, similar to that observed when the water content of the solvent is increased (Fig. 1 vs Fig. 3), although the depth of the pits tends to be diminished in the solvent with a low water content (compare Figs. 2 and 1). In the absence of Span, the product yield from sol A was 50% in Fig. 2, vs 0% in Fig. 1. There were no apparent defects in the thoria microspheres, regardless of whether the solvent was dry or wet (see Figs. 2 and 1). Good yields of UO_2 were obtained in both the dry and the wet solvents in the presence of Span (Table 3). Several of the round UO_2 microspheres are visible in the Span-containing solvents in Figs. 2 and 1, with sol A.

4.6 Statistical Evaluation of the Data

Statistical analyses of the data for two of the ThO_2-UO_3 sols (A and D) and the ThO_2 sol were made. Statistical evaluation was more complex in the present study than for the previous factorial experiment[1] because there was an additional solvent variable (for a total of four) and the additional variable was used at three levels rather than two. Thus the design of the experiment was of the form $3^1 \cdot 2^3$, giving 24 possible solvent compositions. The statistical analysis was performed by the ORNL statistical group, using the Yates algorithm on the IBM 360-75 computer.

The "percent deformed" and "percent cracked" values (Table 3), as well as the severity ratings for deformation and cracking, were tested for the presence of significant effects. The severity ratings were arrived at subjectively and should give a more accurate overall evaluation of sphere quality than the percentages. The percentages are useful as a guide in differentiating the acceptable product from the unacceptable product but do not provide any further information about the severity of the cracking or deformation. Therefore, the products from the sols (except the UO_2 sol) were rated on a basis which included the severity as well as the amount of cracking and deformation. An arbitrary scale of 0 to 10 was employed, the larger numbers signifying a greater degree. The ratings given in Table 3 are the averages of ratings assigned by three observers, from photographs of the products.

The effect coefficients calculated for each of the possible primary and cross effects are listed in Table 4; they are expressed as mean squares. (Statistical analyses were not performed on ThO_2-UO_3 sol G and the UO_2 sol.) The primary Span 80 effect was treated two ways since this variable was present at three levels: as a simple linear effect, and as a possible quadratic effect with both linear and quadratic components. The two latter quantities are shown in parentheses in Table 4. For each group of effect coefficients, the experimental error was estimated in two ways: (1) from the single four-factor interaction, which has two degrees of freedom, and (2) from the pooled four-factor interaction plus the four three-factor interactions, for a total of nine degrees of freedom. Each coefficient was tested against these two error estimates for significance at the 95% confidence level. The results are given in Table 5. The ThO_2 sol is not included since no statistically significant effects were found for it. The three-factor interactions are omitted for the same reason.

The results lead to the following conclusions, based on statistical evaluation of the solvent variables imposed on the three sols:

(1) The ThO_2 sol is not significantly affected by the solvent variables. This statistical conclusion seems to be incompatible with the observations. However, this is a consequence of the limitations inherent in the factorial method. A factorial experiment is designed to detect primary and low-order cross effects; it cannot detect a singular, maximum-order cross effect. For example, Table 4 shows the effect coefficients for the percentage deformation for ThO_2 sol; these figures are derived from input figures of zero percent, which occurs 23 times, and one hundred percent, which occurs once. If the ThO_2 data are correct, then the solvent effects are very complex indeed, and their verification should be carried out by some other technique.

(2) The Span 80 concentration has a significant effect on the cracking and the deformation of the products from both of the ThO_2-UO_3

sols (A and D). This is evident from direct examination of the original data. The statistical significance of this effect therefore puts this conclusion on a quantitative basis.

(3) The Span 80 effect for sol A was a simple linear one; for Sol D, it also had a quadratic component. From our experience with this system as well as related systems, we know that none of these effects, if observed over a wide enough range, will be linear. Thus the presence of a significant quadratic component is not unexpected.

(4) The Ethomeen S/15 concentration had a significant primary effect on the cracking of the products obtained from each of the ThO_2-UO_3 sols. This was anticipated since a similar observation had been made in the previous factorial experiment. Surprisingly, the Ethomeen effect in the present study was found to be significant only with regard to cracking, whereas it was significant for both cracking and deformation in our earlier work. It is true, however, that the earlier effect coefficients for cracking were larger than those for deformation.

(5) Nitric acid concentration had a significant effect on the cracking of the microspheres formed from sol D, although it did not have a similar effect in the prior experiment. Possibly, this was due to an unevaluated variable, such as shaking of the sol in the sample bottle before it was injected into the column. (Shaking of the sol was later demonstrated to cause cracking in product formed from sol D under other conditions.)

(6) A cross effect between the Span 80 and Ethomeen S/15 concentrations significantly affects the cracking of the products of each of the ThO_2-UO_3 sols. This type of effect has been observed in other evaluations, which showed that certain Span 80/Ethomeen S/15 ratios were necessary to obtain good-quality product.

(7) In the case of sol D, cross effects between the Span 80 and the nitric acid concentrations and between the Ethomeen S/15 and the nitric acid concentrations are significant. An Ethomeen S/15 - nitric acid cross effect was also noted in the previous experiment, and is readily explained on the basis of the formation of an amine salt. The

Span 80 - nitric acid cross effect cannot be explained on a similar basis since Span 80 is a neutral, nonionic surfactant. It has been noted, for example, that nitric acid affects the emulsion properties of H_2O - 2EH and H_2O - 2EH - Ethomeen S/15 systems, but not the H_2O - 2EH - Span 80 system.

(8) Without exception, the pooled residual provides a more sensitive test than does the four-factor residual. This is due to the added degrees of freedom.

(9) The two methods of evaluating the products, "percent" and "severity," have no effect on the statistical results derived using the pooled residual but do give greater sensitivity when only the four-factor residual is used. For the purpose of this experiment, the severity rating method is superior to the percentage figures. However, for data with the present degree of scatter, the same effect can be achieved by using a pooled residual.

5. SUMMARY AND CONCLUSIONS

A factorial experiment in forming sol-gel microspheres from ThO_2-UO_3 sols, which was reported previously,[1] was continued. An additional variable and three additional sols were included in the study reported here. The additional variable was the surfactant Span 80 at three concentration levels (0, 0.05, and 0.5 vol %) in the column solvent (2EH). [The previous variables were Ethomeen S/15 concentration (0.05 and 0.5 vol %), water content (0.4 and 1.6 vol %), and nitric acid concentration (0.001 and 0.01 M).] The three additional sols were: (1) a solvent-extracted and digested 80.9% ThO_2 - 19.1% UO_3 sol, (2) a ThO_2 sol prepared by steam-denitration, and (3) a UO_2 sol prepared by the CUSP process. Twenty-four 2EH solvents were used. The data are summarized in Table 3; photomicrographs of the microspheres appear in Figs. 1-8.

The effects of Span 80 were to promote crush-type pitting, which deepened in the more acidic solvents; to reduce clustering; and to reduce Ethomeen-caused pitting and cracking at high Ethomeen S/15 concentration levels. Conversely, Ethomeen S/15 tended to reduce the severity of Span-caused pitting.

Of the sols evaluated in this study, the ThO_2-UO_3 sols were the most sensitive to column conditions with regard to deformation and breakage of product; the steam-denitrated ThO_2 sol was highly resistant; and the UO_2 sol had intermediate resistance, with a tendency to form clusters. The most sensitive of the ThO_2-UO_3 sols was the sol that was prepared without a heated digestion cycle. A less-sensitive sol had been digested for 2 hr to improve crystallinity. The best-quality ThO_2-UO_3 sol, on the other hand, had been prepared by countercurrent solvent extraction and had a lower NO_3^-/metal mole ratio and a higher ThO_2/UO_3 mole ratio; in addition, it had undergone digestion during preparation.

A statistical analysis of the data showed both primary and secondary effects at the 95% confidence level. In the case of ThO_2-UO_3 sols A and D, primary statistical effects due to Span 80, Ethomeen S/15, and nitric acid were found, and secondary or cross effects were seen for Span 80 - Ethomeen S/15, Span 80 - acid, and Ethomeen S/15 - acid. For the ThO_2 sol there were no statistically significant effects (although a singular occurrence, i.e., a four-factor interaction not allowed for in the factorial analysis, clearly did occur). The UO_2 sol and sol G were not evaluated statistically because data for them were incomplete at the time.

Recommended optimum 2EH column conditions for solvent-extracted ThO_2-UO_3 sols tend toward low Ethomeen S/15 levels (0.05 vol %), complete exclusion of Span 80, water concentrations of 0.5 to 1.7 vol %, and a pH range (in the 2EH) of about 3 to 4. Tolerances were much wider for the ThO_2 sol, with the above conditions to be preferred, and a combination of the following conditions to be avoided: 0.05 vol % Ethomeen S/15, 0 to 0.05 vol % Span 80, 0.5 vol % H_2O, and a pH of 0.8. Data for the UO_2 sol, although incomplete, point toward the use of Span 80 to prevent clustering and to good results when Span 80 is mixed with Ethomeen S/15. Factorial experiments using UO_2 sols will be described in later reports.

6. ACKNOWLEDGMENTS

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8. TABLES AND FIGURES

Table 1. Setup for Factorial Experiment in Which Microspheres Were Formed from ThO_2-UO_3, ThO_2, and UO_2 Sols in 2EH

Concentration levels: Ethomeen S/15, 0.05 and 0.5 vol %
HNO_3, 0.001 and 0.01 M
H_2O, 0.5 and 1.7 vol %
Span 80, 0, 0.05, and 0.5 vol %

2EH Solvent	Variable 1, Ethomeen S/15	Variable 2, HNO_3	Variable 3, H_2O	Variable 4, Span 80
1	+	+	+	0, —, +
2	+	+	—	0, —, +
3	+	—	+	0, —, +
4	+	—	—	0, —, +
5	—	+	+	0, —, +
6	—	+	—	0, —, +
7	—	—	+	0, —, +
8	—	—	—	0, —, +

+ indicates high value.

— indicates low value.

0 indicates zero level.

Table 2. Sols Used in Span 80 - Ethomeen S/15 Factorial Experiment

	Sol			
	A	D	G	GS-26
Composition	75% ThO_2 - 25% UO_3	75% ThO_2 - 25% UO_3	80.9% ThO_2 - 19.1% UO_3	ThO_2
Molarity	2.3	2.1	~1.2	3.0
NO_3^-/metal atom ratio	0.12	0.12	0.07	0.10
Digestion time, hr	0	2	1-2	—
Preparation method	Cocurrent solvent extraction	Cocurrent solvent extraction	countercurrent solvent extraction	Steam denitratio[n]

ɔle 2. Sols Used in Span 80 - Ethomeen S/15 Factorial Experiment

Sol				
A	D	G	GS-26	CUSP-7
$)_2$ - 25% UO_3	75% ThO_2 - 25% UO_3	80.9% ThO_2 - 19.1% UO_3	ThO_2	UO_2
	2.1	∿1.2	3.0	1.4
	0.12	0.07	0.10	0.11
	2	1-2	—	—
ɪnt solvent ;ion	Cocurrent solvent extraction	countercurrent solvent extraction	Steam denitration	CUSP process

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Table 3. Defects and Yie

	Solvent Composition					ThO_2-UO_3 Sol (Sol A)					ThO_2-UO_3 Sol		
						Deformed Product		Cracked Product			Deformed Product		Crac Proc
Solvent No.	Ethomeen S/15 (vol %)	Span 80 (vol %)	H_2O (vol %)	HNO_3 ($\underline{M}$)	pH	%	Severity	%	Severity	Product Yield (%)	%	Severity	%
1	0.5	0	1.7	0.01	2.0	100	7	100	8	0	10	2	20
	0.5	0.05	1.7	0.01		50	3	90	6	0	0	0	50
	0.5	0.5	1.7	0.01		100	8	100	7	0	100	9	50
2	0.5	0	0.5	0.01	1.8	0	0	50	4	50	5	1	5
	0.5	0.05	0.5	0.01		10	1	90	6	10	25	2	50
	0.5	0.5	0.5	0.01		100	8	100	9	0	100	8	15
3	0.5	0	1.7	0.001	7.3	100	3	100	7	0	5	1	0
	0.5	0.05	1.7	0.001		100	4	100	9	0	100	8	100
	0.5	0.5	1.7	0.001		100	4	100	9	0	100	9	100
4	0.5	0	0.5	0.001	6.7	100	5	100	9	0	100	5	2
	0.5	0.05	0.5	0.001		100	5	100	10	0	100	7	100
	0.5	0.5	0.5	0.001		100	5	100	10	0	100	8	100
5	0.05	0	1.7	0.01	1.0	0	0	0	0	98	0	1	0
	0.05	0.05	1.7	0.01		100	10	0	0	0	100	10	0
	0.05	0.5	1.7	0.01		100	9	50	6	0	100	9	0
6	0.05	0	0.5	0.01	0.8	100	4	5	1	0	100	4	5
	0.05	0.05	0.5	0.01		100	9	5	1	0	100	7	0
	0.05	0.5	0.5	0.01		100	10	100	8	0	100	9	25
7	0.05	0	1.7	0.001	3.8	0	0	10	1	90	0	0	0
	0.05	0.05	1.7	0.001		100	7	25	2	0	100	5	0
	0.05	0.5	1.7	0.001		100	9	80	8	0	100	8	100
8	0.05	0	0.5	0.001	3.7	0	0	25	2	75	0	0	1
	0.05	0.05	0.5	0.001		100	2	0	2	0	100	4	0
	0.05	0.5	0.5	0.001		100	8	50	4	0	100	8	50

[a] UO_2 breakage was probably caused by oxidation in air.

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ıd Yields of Microspheres in Factorial Experiment

O_3 Sol (Sol D)			ThO_2-UO_3 Sol (Sol G)					ThO_2 Sol					
Cracked Product		Product Yield	Deformed Product		Cracked Product		Product Yield	Deformed Product		Cracked Product		Product Yield	
%	Sever-ity	(%)	%	Sever-ity	%	Sever-ity	(%)	%	Sever-ity	%	Sever-ity	(%)	Observ
20	2	75	100	3	25	3	0	0	0	0	0	100	Cluste
50	4	50	1	1	15	4	85	0	0	0	0	100	Broken
50	5	0	100	6	5	8	0	0	0	0	0	100	Broken
5	1	90	0	0	95	2	3	0	0	0	0	100	Cluste
50	4	50	0	0	10	4	90	0	0	0	0	100	Cluste
15	2	0	0	0	75	8	30	0	0	0	0	100	Cracke
0	1	95	0	0	50	8	50	0	0	1	0	99	Cluste
100	10	0	0	0	10	3	90	0	0	0	0	100	Cluste
100	10	0	0	0	2	1	98	0	0	1	0	99	Broken
2	1	0	0	0	50	3	50	0	0	2	1	98	Cluste
100	9	0	0	0	30	3	70	0	0	15	3	85	Broken
100	10	0	0	0	5	1	95	0	0	5	2	95	Broken
0	0	100	0	0	100	9	0	0	0	0	0	100	—
0	0	0	100	7	0	0	0	0	0	0	0	100	—
0	2	0	100	9	0	0	0	0	0	0	0	100	—
5	0	0	0	0	75	9	25	0	0	100	9	0	—
0	0	0	100	4	1	7	0	0	0	75	7	25	—
25	2	0	100	8	2	7	0	0	0	0	0	100	—
0	0	100	0	0	0	0	100	0	0	0	0	100	Cluste
0	0	0	20	2	1	8	80	0	0	1	0	99	Slight
100	7	0	100	4	0	0	0	0	2	0	0	100	Small
1	0	99	0	0	0	0	100	0	0	0	0	100	Broken
0	0	0	25	2	0	0	75	0	0	1	0	99	Broken
50	5	0	100	4	0	0	0	100	(3)	0	0	(100)	

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G)	ThO$_2$ Sol					UO$_2$ Sol	
	Deformed Product		Cracked Product				
Product Yield (%)	%	Sever-ity	%	Sever-ity	Product Yield (%)	Observed Defects[a]	Product Yield (%)
0	0	0	0	0	100	Clustered, broken	50
85	0	0	0	0	100	Broken	75
0	0	0	0	0	100	Broken	95
3	0	0	0	0	100	Clustered	90
90	0	0	0	0	100	Clustered	90
30	0	0	0	0	100	Cracked	95
50	0	0	1	0	99	Clustered, chipped	80
90	0	0	0	0	100	Clustered, broken	50
98	0	0	1	0	99	Broken	50
50	0	0	2	1	98	Clustered, chipped	20
70	0	0	15	3	85	Broken	40
95	0	0	5	2	95	Broken	50
0	0	0	0	0	100	—	—
0	0	0	0	0	100	—	—
0	0	0	0	0	100	—	—
25	0	0	100	9	0	—	—
0	0	0	75	7	25	—	—
0	0	0	0	0	100	—	—
100	0	0	0	0	100	Clustered, broken	25
80	0	0	1	0	99	Slightly clustered	95
0	0	2	0	0	100	Small pits	95
100	0	0	0	0	100	Broken	75
75	0	0	1	0	99	Broken	99
0	100	(3)	0	0	(100)		99

Table 4. Statistical Evaluation of Data for ThO_2-UO_3 Sols A and D, and for the ThO_2 Sol in Terms of Mean Squares of the Various Effect Coefficients

	ThO_2-UO_3 Sol A				ThO_2-UO_3 Sol D				ThO_2 Sol			
	Deformation		Cracking		Deformation		Cracking		Deformation		Cracking	
	%	Severity	%	Severity	%	Severity	%	Severity	%	Severity	%	Severity
Primary Effects												
1. Span 80	5150	55	3279	62	11064	92	5345	46	417	1	353	3
(Linear component)	(6976)	(89)	(6553)	(62)	(13857)	(144)	(7172)	(68)	(826)	(2)	(705)	(5)
(Quadratic component)	(3324)	(21)	(5)	(0)	(8270)	(39)	(3517)	(23)	(7)	(0)	(0)	(0)
2. Ethomeen S/15	150	9	25350	145	1001	1	7038	77	417	1	975	4
3. Nitric acid	817	12	417	12	1134	0	4620	40	417	1	925	4
4. Water	67	2	38	0	1926	0	187	2	417	0	1584	20
Cross Effects												
1 x 2	3650	25	1888	11	1439	6	2640	16	417	1	343	3
1 x 3	817	1	317	3	1353	2	2586	15	417	1	338	3
1 x 4	67	2	88	0	1333	3	135	1	417	0	353	3
2 x 3	4817	9	67	5	5551	40	145	9	417	1	1617	20
2 x 4	2400	0	204	0	9	0	35	0	417	0	1001	4
3 x 4	67	0	104	0	26	0	30	0	417	0	1001	4
1 x 2 x 3	1317	13	17	1	1395	12	482	5	417	1	341	3
1 x 2 x 4	1400	7	254	3	41	2	12	0	417	0	338	3
1 x 3 x 4	67	2	629	6	26	1	96	0	417	0	338	3
2 x 3 x 4	2400	22	938	7	1276	0	715	1	417	0	1584	20
Residuals[a]												
1 x 2 x 3 x 4	1400	3	88	1	1901	6	427	1	417	0	353	3
Pooled	1196	8	324	3	889	4	305	1	417	0	480	5

[a]Error estimates.

Table 5. Significant Effects[a] in Table 4 (Tested at the 95% Confidence Level)

	ThO_2-UO_3 Sol A				ThO_2-UO_3 Sol D			
	Deformation		Cracking		Deformation		Cracking	
	%	Severity	%	Severity	%	Severity	%	Severity
Primary Effects								
1. Span 80	1	+	+	+	1	+	1	+
(Linear component)	1	+	+	+	1	+	1	+
(Quadratic component)					1	1	1	+
2. Ethomeen			+	+			1	+
3. Nitric acid							1	+
4. Water								
Cross Effects								
1 x 2			+				1	1
1 x 3							1	1
1 x 4								
2 x 3					1	1		1
2 x 4								
3 x 4								

[a]"+" significant in both tests: against the 1 x 2 x 3 x 4 residual and against the pooled residual.
"1" significant only when tested against the pooled residual.

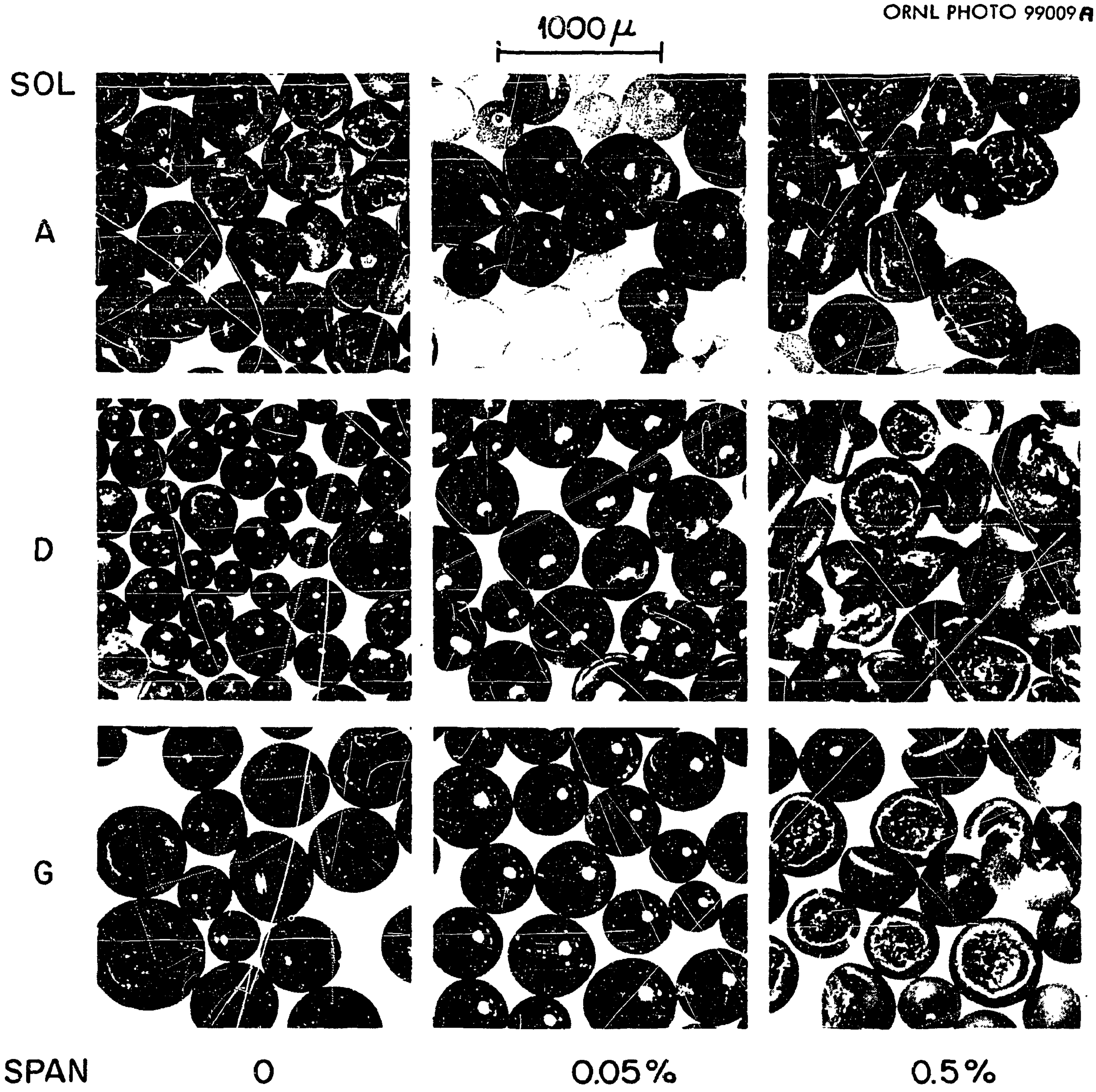

Fig. 1. Microspheres Formed in Solvent 1.

Ethomeen S/15 . . .	0.5%
HNO_3	0.01 M
H_2O	1.7%
pH	2.0

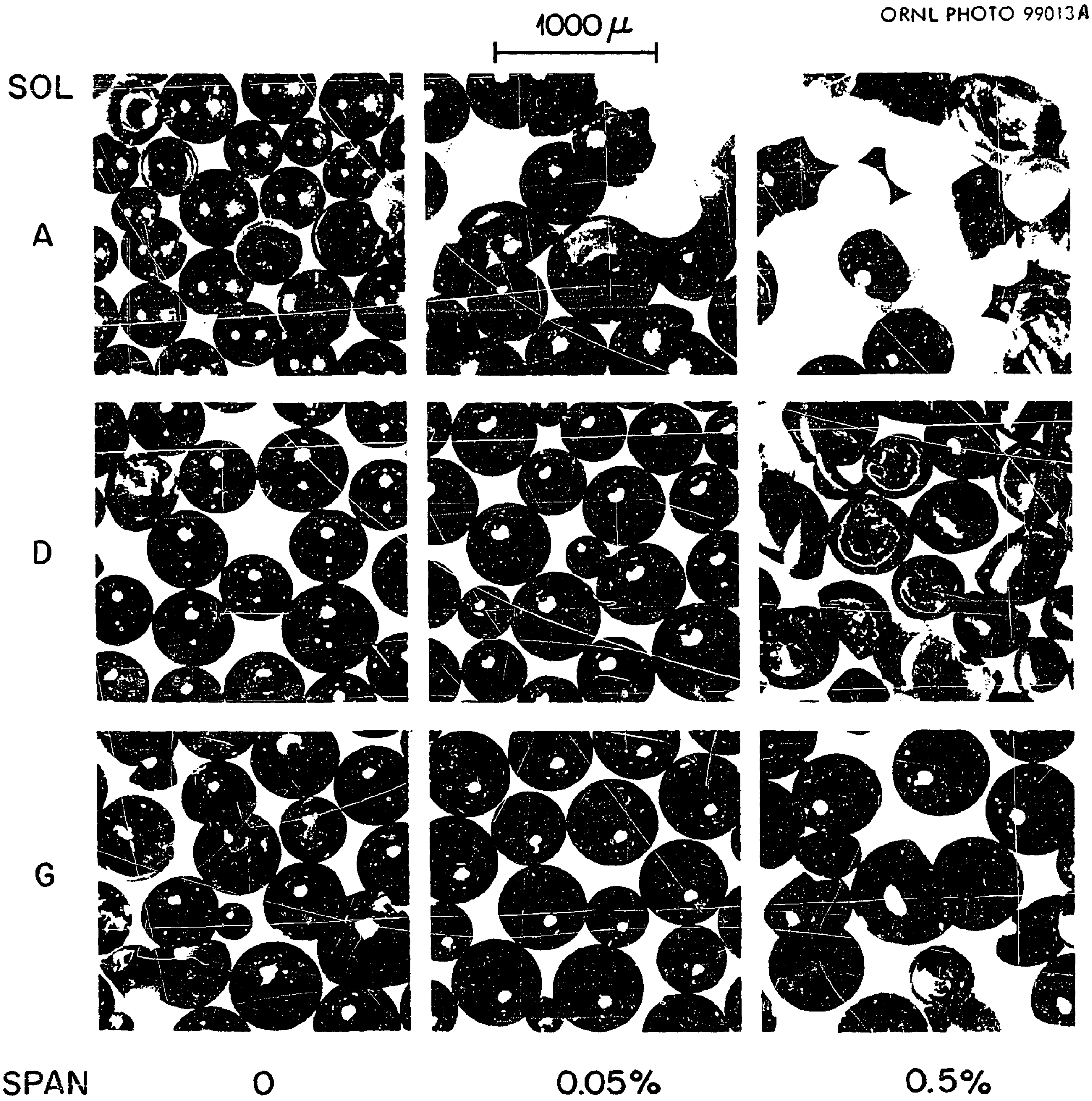

Fig. 2. Microspheres Formed in Solvent 2.

Ethomeen S/15 . . . 0.5%
HNO_3 . . . . 0.01 M
H_2O 0.5%
pH 1.8

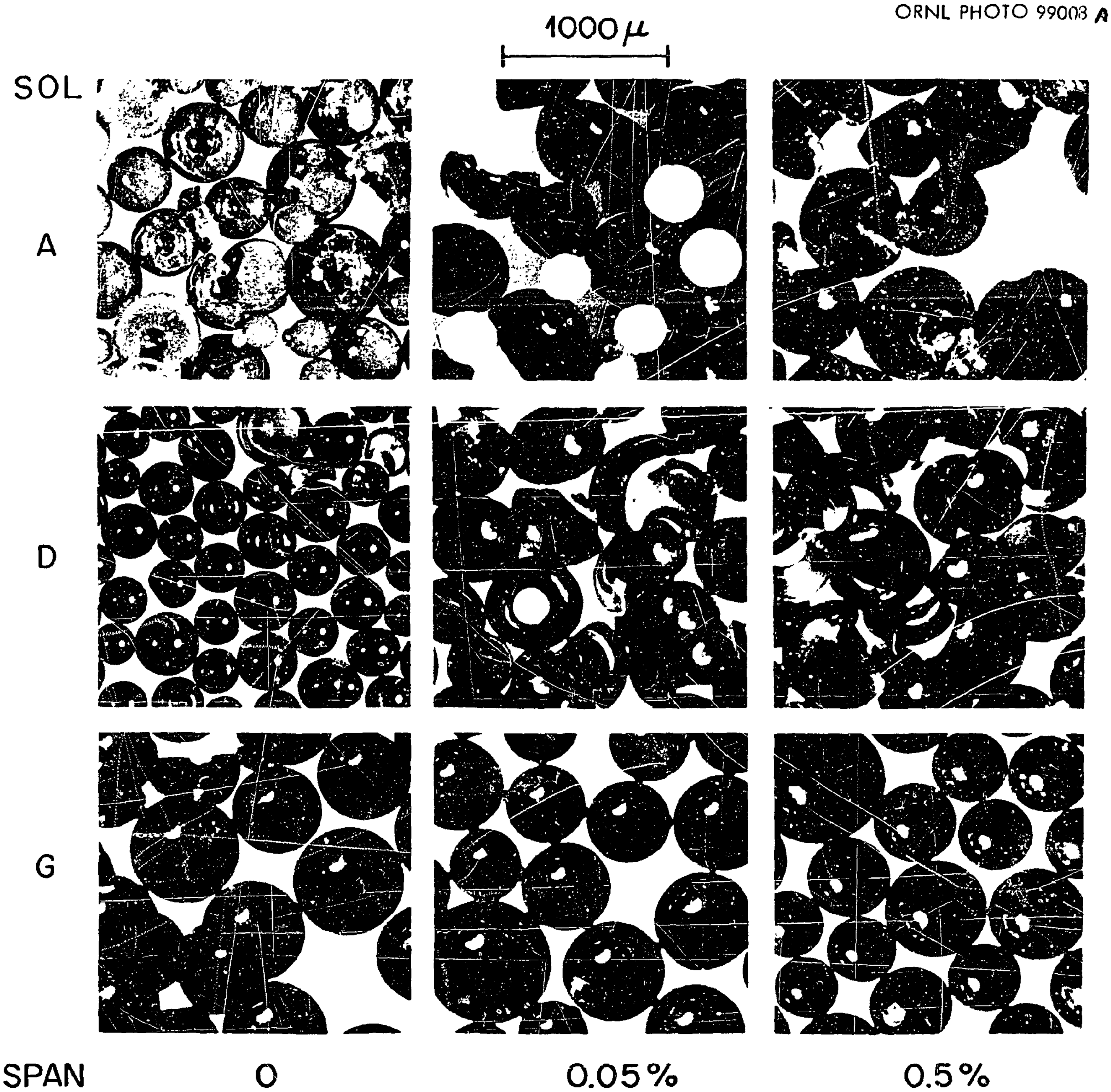

Fig. 3. Microspheres Formed in Solvent 3.

Ethomeen S/15 . . . 0.5%
HNO_3 . . . . 0.001 M
H_2O 1.7%
pH 7.3

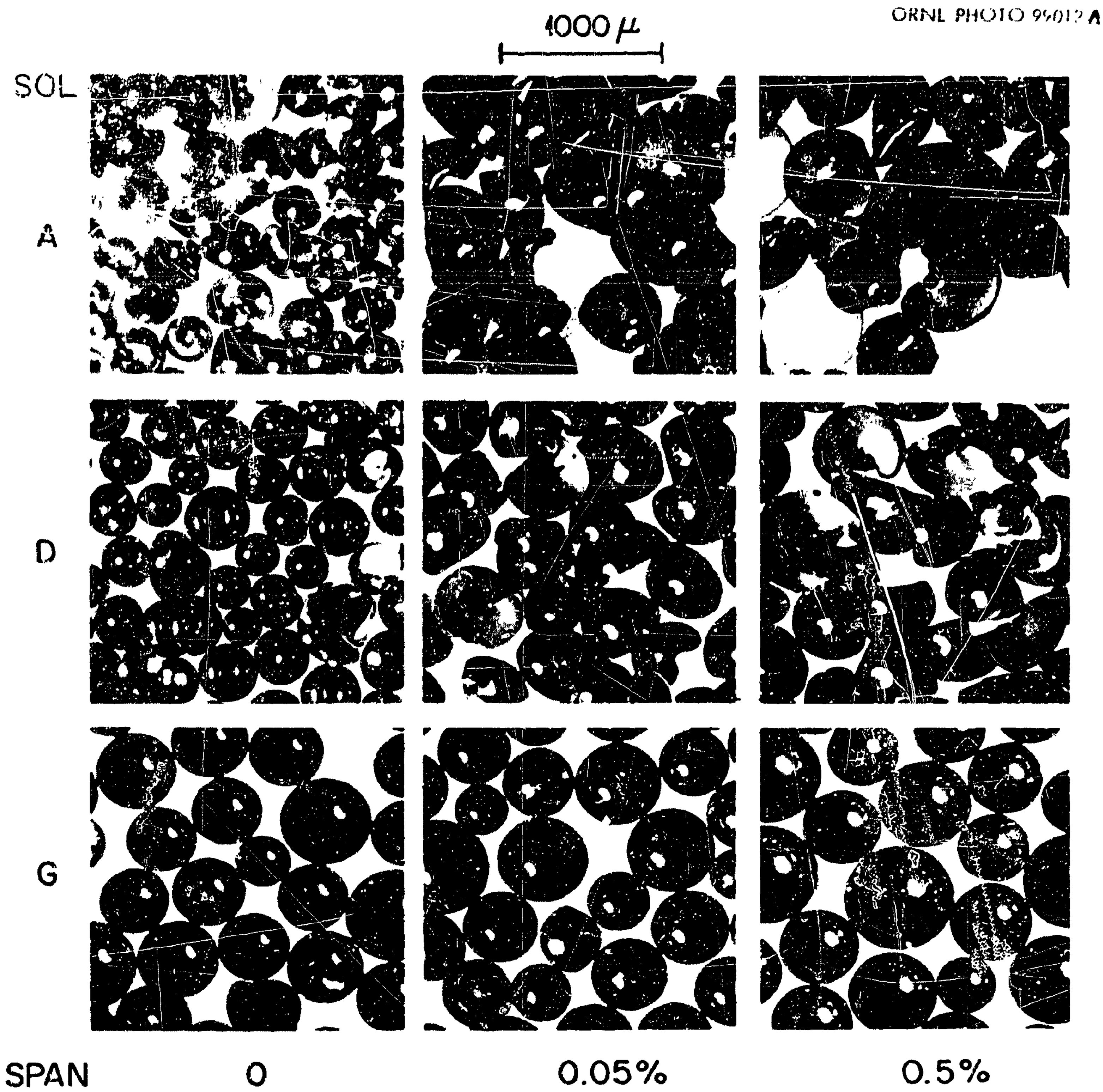

Fig. 4. Microspheres Formed in Solvent 4.

Ethomeen S/15 . . .	0.5%
HNO_3	0.001 M
H_2O	0.5%
pH	6.7

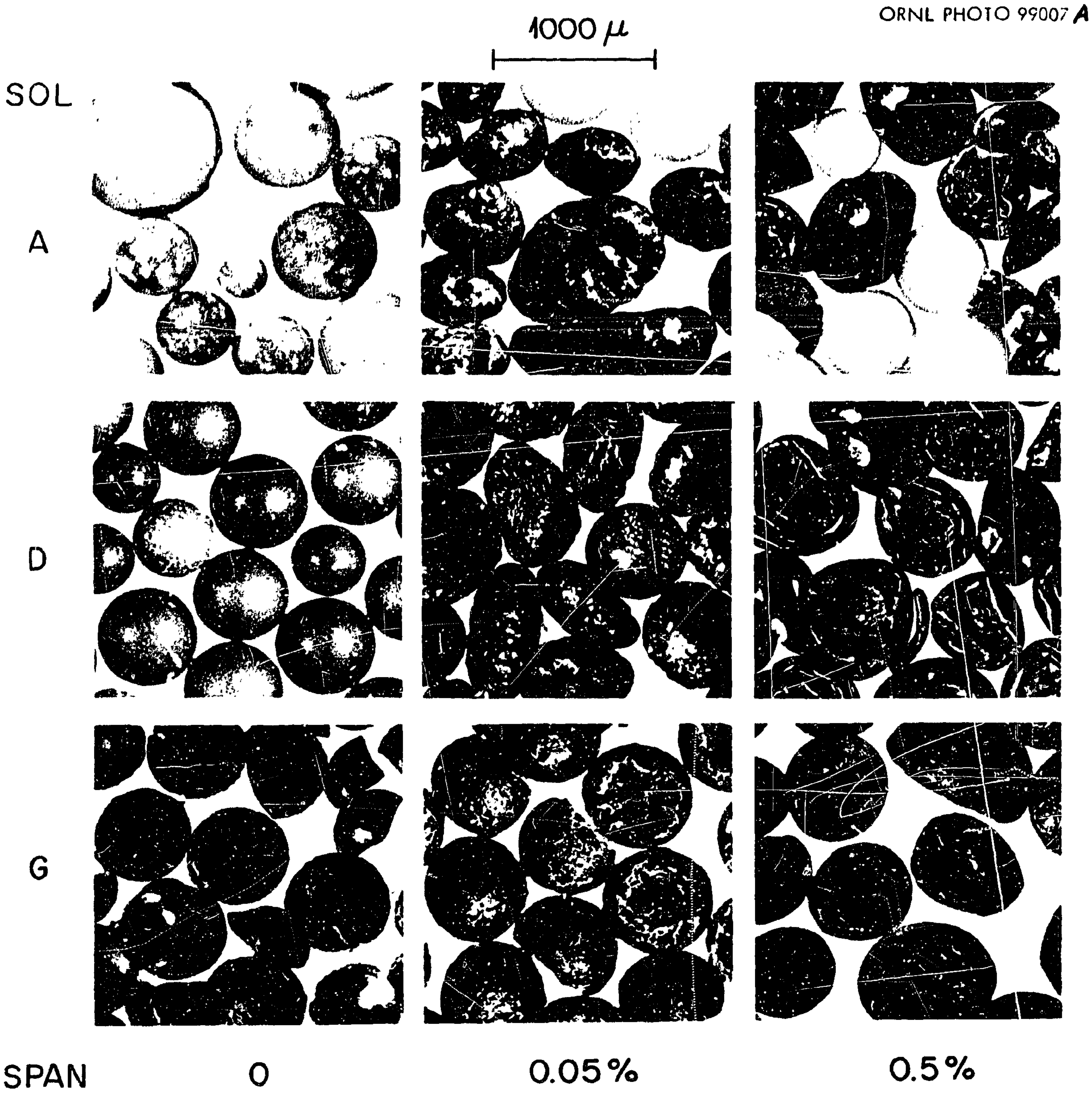

Fig. 5. Microspheres Formed in Solvent 5.

Ethomeen S/15 . . . 0.05%
HNO_3 . . . . 0.01 M
H_2O 1.7%
pH 1.0

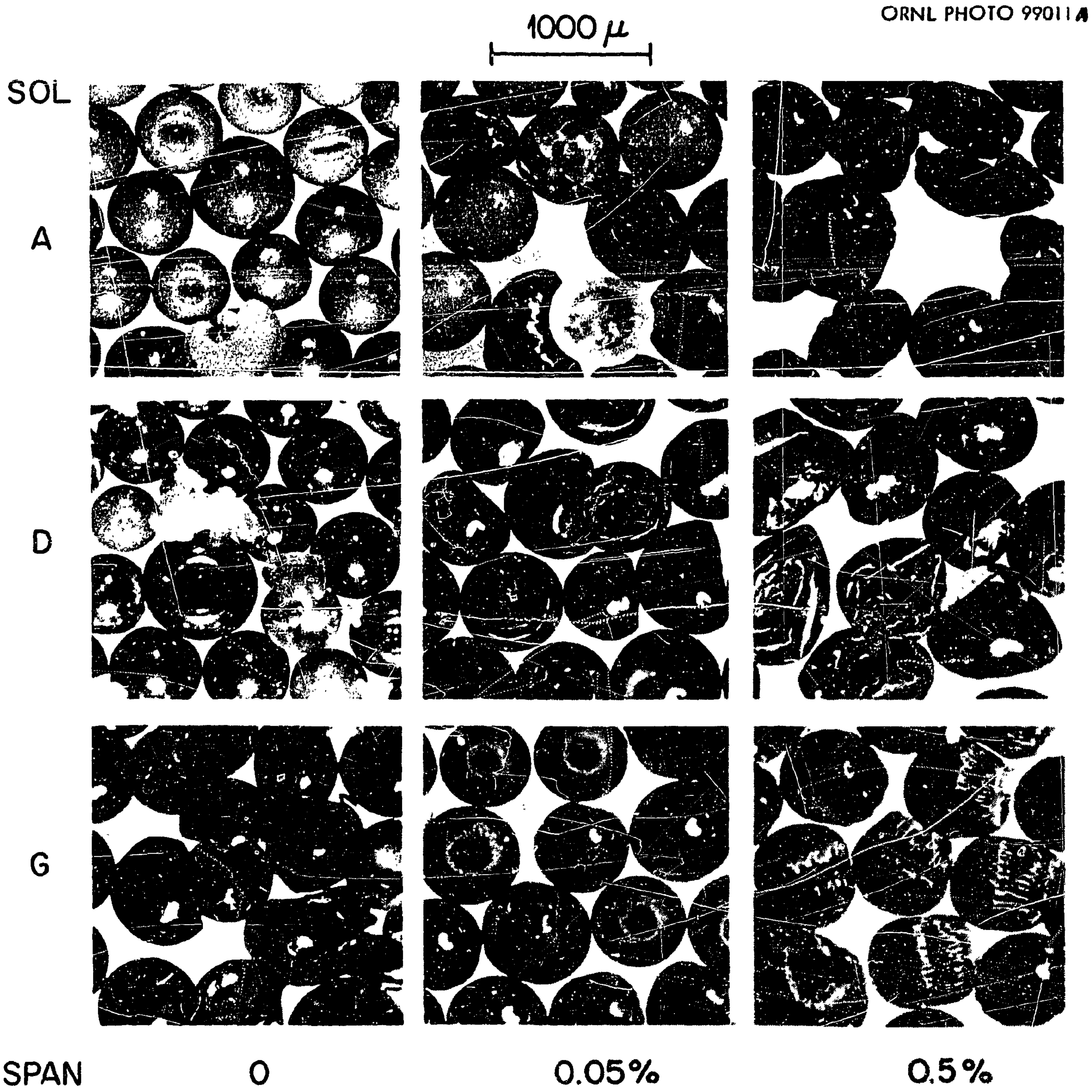

Fig. 6. Microspheres Formed in Solvent 6.

Ethomeen S/15 . . .	0.05%
HNO_3	0.01 M
H_2O	0.5%
pH	0.8

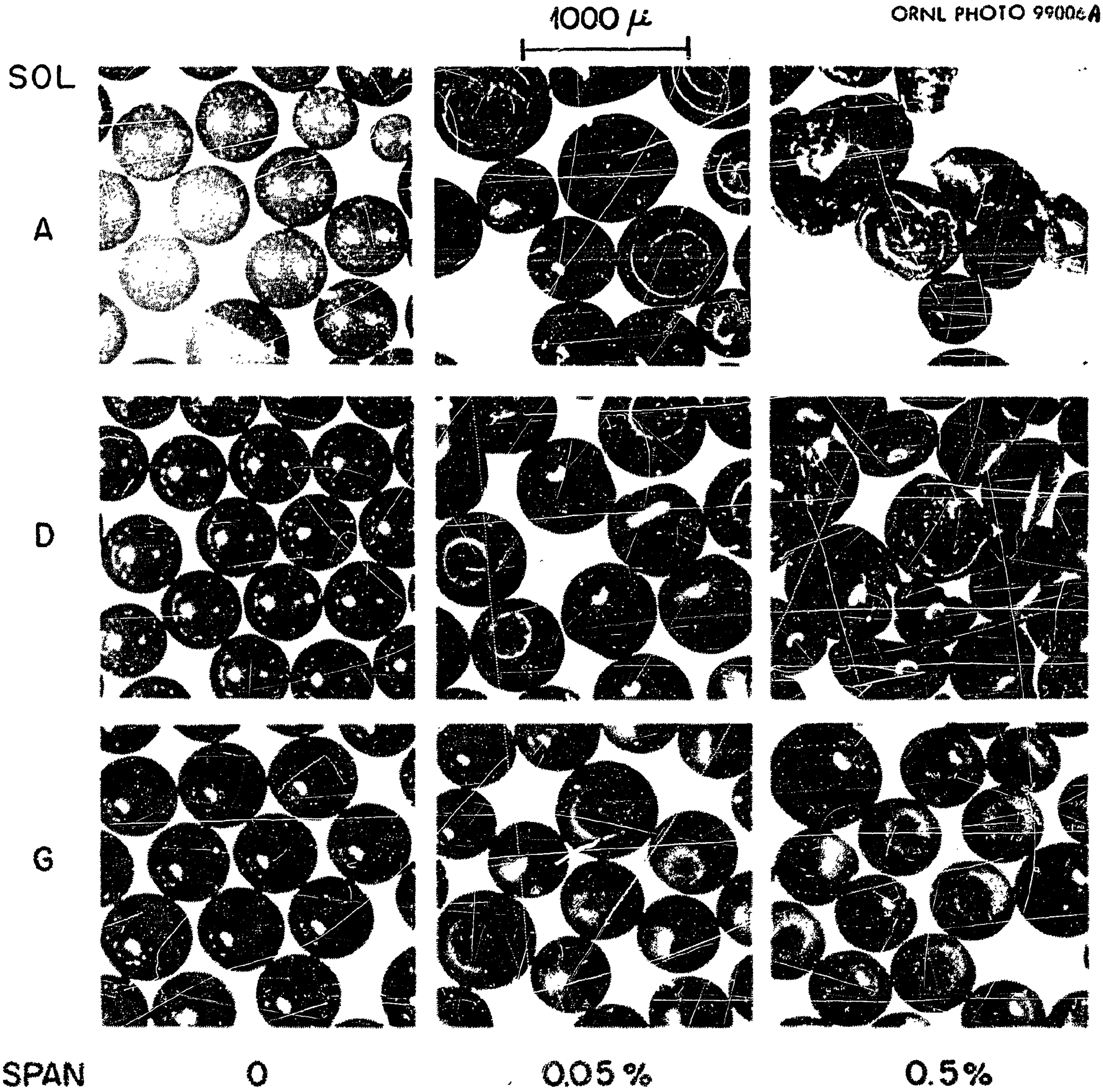

Fig. 7. Microspheres Formed in Solvent 7.

Ethomeen S/15 . . .	0.05%
HNO_3	0.001 <u>M</u>
H_2O	1.7%
pH	3.8

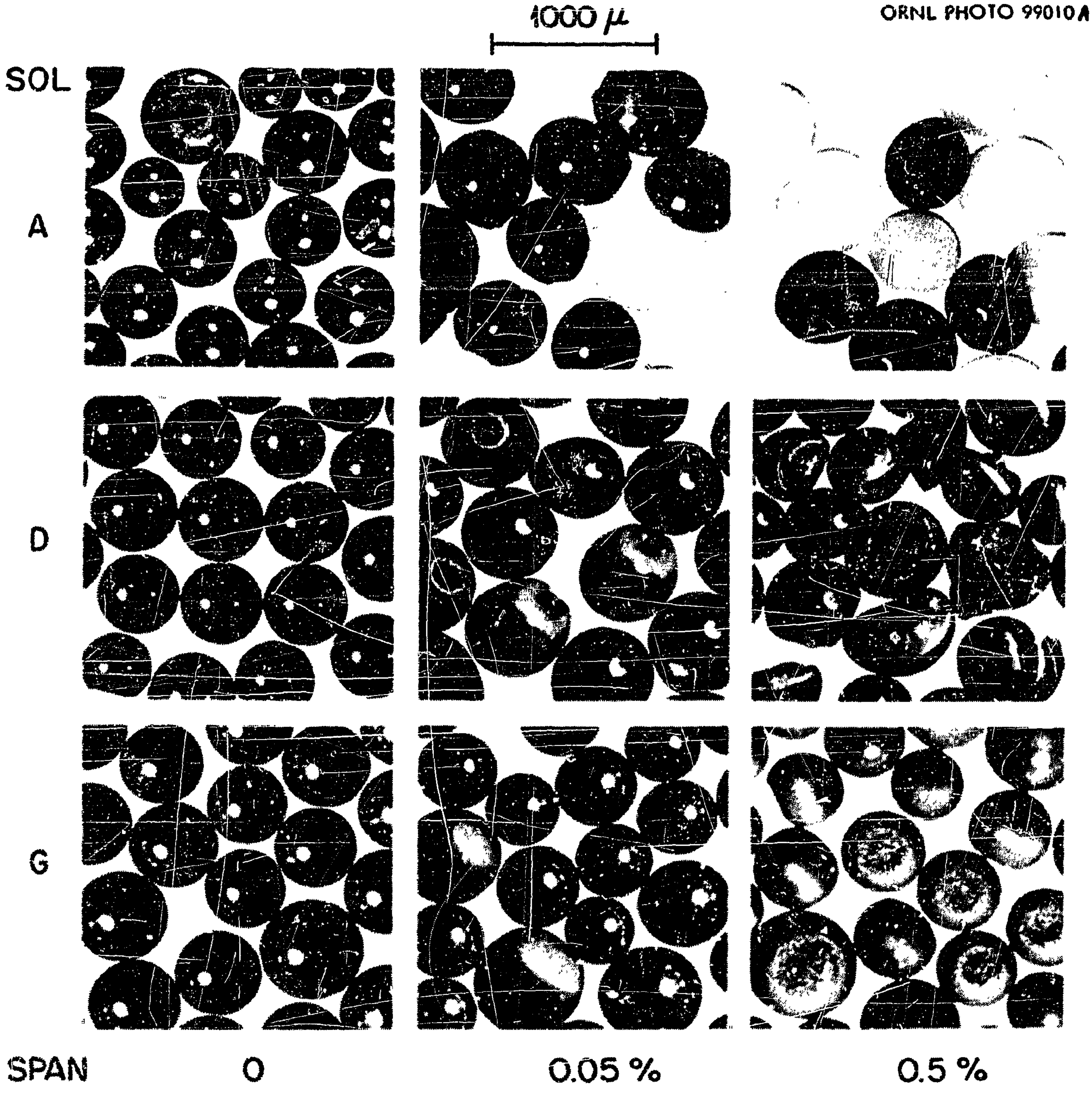

Fig. 8. Microspheres Formed in Solvent 8.

Ethomeen S/15 . . .	0.05%
HNO_3	0.001 M
H_2O	0.5%
pH	3.7