

Part VII. Special applications II

GENERATION OF SiO₂-MEMBRANES FROM ALKOXYSILANES ON POROUS SUPPORTS

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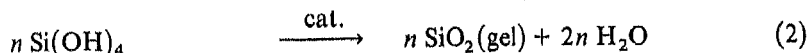
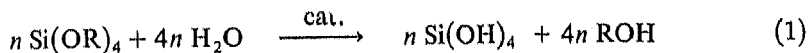
Siliceous membranes were brought onto the surface of filter media to improve their filtration properties. Using the sol-gel method, membranes with various shapes and properties could be reacted directly into a narrow surface region without bringing condensation products into the volume of the porous supports. A belt of filter media could be coated continuously and homogeneously using laboratory scale equipment. The coated filter media showed improved cleaning behaviour compared to uncoated samples.

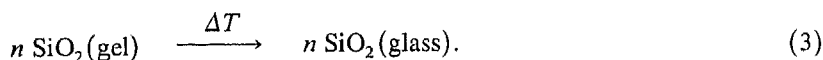
1. Introduction

Usually membranes are defined as thin liquid or solid films where matter, electrical charges or heat can penetrate through [1]. A more general definition says, a membrane is a selective separating region of a certain thickness, the stationary phase of which may contain pores of various diameters or, in the case of supported membranes, the single elements do not necessarily have to be connected to each other [2]. In this paper we will follow the latter definition. The technical applications of membranes (e.g. reversed osmosis, filtration techniques) are becoming more and more important [3,4], but the number of technical uses is often limited by material properties. In most cases membranes are made from organic materials such as cellulose derivatives and therefore they show low resistance against higher temperatures and organic solvents.

With respect to these properties membranes based on inorganic materials may have some advantages. Such membranes can be prepared by the sintering of metal powders [5] or by the well known preparation of porous glasses [6,7] or of porous porcelain [8]. The idea of preparing membranes in the shape of discs by the sol-gel method from Si(OR)₄ was published in 1928 by Dearing and Reid [9], but they did not succeed in synthesizing specimens suitable for planned osmotic pressure measurements. Later, thin films as coatings on nonporous supports were made by the sol-gel method [10-12].

The general reaction from alkoxy silanes to SiO₂ involves at least three steps: hydrolysis, condensation and densification, e.g. glass formation [eqs. (1)-(3)].





To prepare membranes by the sol-gel process, densification according to eq. (3) is not necessary. Intermediates, still soluble in organic solvents, can be obtained when the hydrolysis and condensation reaction is not completed. This allows the use of known membrane preparation techniques like casting or spraying, and in case of preparing bulk materials, the cutting off of thin discs becomes possible. Additionally the sol-gel process allows the formation of membranes during the polymer synthesis.

One possible application of such membranes should be the coating of filter media to improve the filtration properties. This paper reports on investigations to verify that suggestion. According to that application the main point of judgement and of characterization of the membranes has been the variation of filtration characteristics.

2. Synthesis of SiO₂-membranes on porous supports

2.1. Problems

Separations of particulate matter from liquid or gaseous media by filtration are mostly performed using a deep bed filter. This type of filter displays an open structure, and the particles to be separated will be retained in the volume of the filter. This leads to an irreversible clogging of the filters and, if the pressure drop becomes intolerable, the filter media have to be removed. Technical applications with prolonged shelf life (e.g. dust separation in contaminated production departments) require filters with further properties. Such properties may be derived from asymmetric cellulose acetate membranes or from composite membranes with a thin film of an organic polymer on a porous support. By such means, the deep bed type filtration may be converted into a surface type. However, difficulties arise by attaching this type of membrane to the carrier, since in the case of dust filtration, the regeneration has to be performed e.g. by a pressure shock from the clean gas side. The problems related to the handling of such thin films and to the adhesion of the membrane to the support might be overcome by reacting the membrane directly onto the support during synthesis.

To perform this "reactive coating" by the hydrolysis and condensation reaction of alkoxysilanes [eqs. (1) and (2)], a technique had to be developed to face the problem of covering the free space between the fibers of the supporting tissue (fig. 1). To obtain a membrane of desired shape, it was necessary to react the silane very rapidly in a narrow zone at the surface of the support so that no diffusion and further penetration of reactive intermediates into the volume of the filter medium became possible.

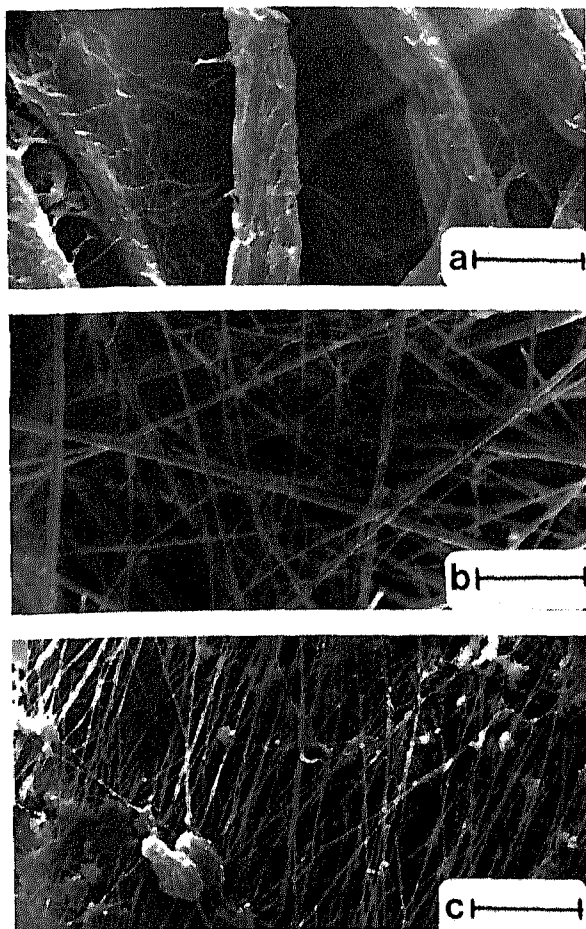


Fig. 1. Scanning electron micrograph (SEM) of the structure of deep bed filter media. a. paper filter. b. glass fiber fleece. c. polyester felt. (length of the bars: $20 \mu\text{m}$).

2.2. Liquid phase reaction

Following known reaction principles, the desired narrow reaction zone was generated in the interface between two immiscible phases, one containing the silane (and perhaps a solvent), the other one containing water and a catalyst (e.g. acid or base). Hydrolysis could only occur in the boundary layer where both water and silane were present. The support had to be fixed in the system in such a way that its surface was placed in the boundary layer between the two phases (see fig. 2).

The shape and the properties of the membranes obtained with this laboratory equipment can be influenced by various reaction parameters. In table 1

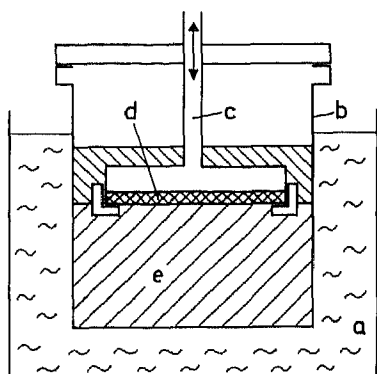


Fig. 2. Scheme of the laboratory membrane preparation equipment. a. thermostat. b. reaction chamber. c. support holder (vertically movable). d. support. e. 2-phases reacting system.

some of the most important parameters are summarized, together with the properties influenced by them.

It is known from the literature [13,14] that increasing the length of the organic chain R of tetraalkoxysilanes decreases the hydrolysis rate. As expected from that, tetraethoxysilane reacted significantly slower in the two phase system than tetramethoxysilane. Only water immiscible organic liquids like carbon tetrachloride are useful as solvents for the silane. Increasing solvent/silane ratios lead to lower reaction rates, therefore these ratios should not exceed 2:1. Increasing reaction times result in thicker membranes. A temperature of about 25°C is sufficient, higher temperatures accelerate the reaction, but make it more difficult to get a homogeneous membrane with reproducible properties. The highest temperature used was 60°C . The most important reaction parameter in this system is the catalyst. While ammonia as catalyst makes it very difficult to obtain condensation products only in the desired surface zone of the support, hydrochloric acid provides better results, if used in concentrations of 6 mol./l or higher.

Generally, a suitable membrane only is built up, if the reaction of hydrolysis

Table 1

List of reaction parameters and membrane properties influenced by them

Reaction parameters	Membrane properties
Silane (kind of alkoxy groups and concentration)	Membrane thickness
Catalyst (kind and concentration)	Porosity
Solvent	Mean pore diameters (conditioning)
Reaction time	permeability and cut off size)
Temperature	Mechanical properties (e.g. strength, flexibility)

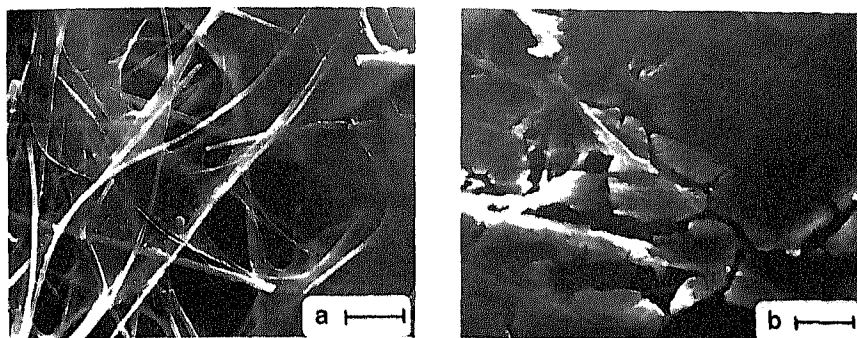


Fig. 3. Scanning electron micrographs of two examples of membranes obtained from liquid phase reaction. a: catalyst concentration low; b: catalyst concentration high (length of the bars: 10 μm).

and condensation occurs within a few minutes. If the reaction rate becomes too low, a gradual diffusion of water into the silane phase takes place, leading to the gelation of the entire phase volume, whereas gelation in the aqueous phase cannot be observed. The best membranes are obtained from $\text{Si}(\text{OCH}_3)_4$ in CCl_4 (volume ratio solvent : silane = 1 : 1) using 6 mol./l HCl as catalyst at temperatures between 25°C and 40°C.

As shown in the scanning electron micrographs of fig. 3, this preparation technique allows the synthesis of membranes onto supports with significantly different appearance. The advantages of this technique are good reproducibility of the reaction conditions and the possibility to use all the variabilities of the sol-gel method. The photographs, however, also show one disadvantage of this technique: though in the laboratory experiments only an area of about 10 cm^2 was clamped into the support holder, spots with incomplete covering always appear. This incomplete coverage could not be avoided, because it was extremely difficult to place the surface of the substrate exactly into the boundary layer, especially when larger areas had to be coated. A variation of the method, where the support was soaked with an aqueous catalyst and then placed onto the surface of the silane bath, gave only little improvement.

For large scale production of "reactive coated" filters, however, it is indispensable to produce homogeneous membranes with constant thickness and sufficient support coverage. Therefore another preparation technique was used to meet these demands.

2.3. Vapour phase reaction

The vapour phase reaction is another way to restrict the hydrolysis and condensation reaction to a narrow zone at the support surface. The advantage of this technique should be that it is no longer necessary to place the support into a phase boundary. In this case the reactands may be transported consecutively to the support, either each of them via gas phase or only one of them as a

vapour, when the support first is loaded with the other one. Experimental results, however, show that in the first case, independent of the chronological sequence, the restriction of the silane condensation and gelation only to the support surface is not possible. Either the covering of the surface is insufficient or large parts of the filter volume are clogged by the condensation product.

Better results should be achievable by a two step reaction. At first the support has to be filled with water and catalyst and in a second step the pretreated support must be exposed to a well defined silane vapour pressure. If it is possible to reach condensation and gelation rates fast enough to avoid penetration of reactive intermediates into the filter volume, it should be possible to build up membranes on the surface of the support. It could be proved experimentally that the best membrane formation occurred, when the support was soaked with an aqueous catalyst (by preference hydrochloric acid) and placed above the silane bath. The partial vapour pressure of the silane can be altered by the bath temperature and its concentration in the solvent. The most efficient parameter was the silane partial pressure. The catalyst concentration was less effective than in the liquid reaction system described above. Table 2 summarizes the reaction conditions and a short characterization of the resulting membranes obtained from a series of experiments with this method.

Much more homogeneous covering of the substrate could be obtained by this method than in the previous experiments. The wide variability of the properties of the resulting membranes including very thin films stretched between the fibers of the tissue and torn layers of some μm thickness is shown in fig. 4. Most astonishing is the fact that shrinking does not lead to cracking of the layers, if they are thin enough. According to the reaction scheme [eqs. (1) and (2)], as a consequence of the loss of water during the crosslinking

Table 2

Reaction conditions and membrane characterization of vapour phase experiments (silane: Si(OCH₃)₄; no solvent)

No.	HCl concentration (mol./l)	Silane temperature (°C)	Exposition time (min)	Membrane characterization
1	2	25	15	few condensate in the volume, no membrane
2	2	45	15	≈ 1 μm thick, not torn, beyond the upper fiber layer, coverage > 90%
3	2	45	25	≈ 3 μm thick
4	6	25	15	partial coverage (≈ 70%), not torn
5	6	45	15	≈ 3 μm thick, coverage ≈ 90%, partially torn
6	6	45	25	≈ 10 μm thick, torn, homogeneous, coverage (> 90%)
7	12	25	15	partial coverage, no continuous membrane

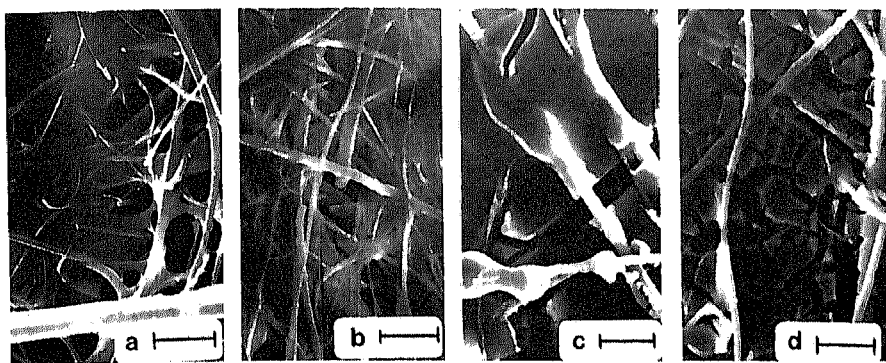


Fig. 4. Scanning electron micrographs of some membranes (see table 3) obtained from vapour phase reaction (length of the bars: $10 \mu\text{m}$).

reaction, shrinking must be expected. The drying procedure in this case does not play a very important role as expected from preparing monolithic materials by the sol-gel process. Slow drying at room temperature leads to almost the same product properties as drying at temperatures up to 120°C . On the other hand, thicker membranes show shrinkage accompanied by tearing, even if they are dried very slowly at room temperature. The SEM of a cross section of a membrane coated filter in fig. 5 shows that it is possible to restrict the condensation reaction to a very narrow region of only a few μm thickness or less at the substrate surface, while the volume of the filter medium remains completely free from condensation products.

Using these reaction principles, a continuous coating technique was developed. An endless belt of the support is transported through a bath of aqueous HCl , exposed to a silane vapour phase in a special chamber and dried. The main parameters to influence the membrane performance and properties are

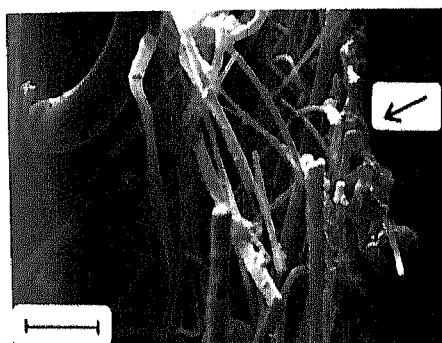


Fig. 5. Scanning electron micrograph of a cross section of a membrane coated filter medium; the arrow indicates the surface (length of the bar: $10 \mu\text{m}$).

the temperature of the silane bath and the belt velocity, whereas the concentration of HCl and the distance between bath and belt are less critical. A silane temperature of about 40°C , an exposition time of 10–20 min and HCl concentrations of 2–12 mol./l are sufficient to produce improved membranes.

3. Influence of the membrane on the filtration properties of coated filter media

As outlined above, the main rating criterion for the membranes developed during this investigation is the improvement of the filter process with respect to the regeneration of the filter medium. Contrary to many other membrane applications the question of selectivity is not critical in this case, since even with the uncoated filter, by the substrate's action as a deep bed filter, the demands of dust prevention are met. The membrane should mainly change the filter characteristic from a deep bed into a surface type filter and thus, by improving regeneration, increase the service life significantly. However, the membranes must not heighten the flow resistance of the filter too much and must show a sufficient stability to withstand the necessary cleaning procedure (e.g. pressure shock from the uncoated side and/or vibrations).

Therefore the membranes were characterized by measuring the change of pressure drop through the filter caused by the membrane coating and the loss of permeability during a multiple dust loading and cleaning procedure. The properties of a glass fiber fleece are changed significantly by a membrane coating: the initial pressure drop increases generally, the extent depends on the membrane thickness and the degree of surface coverage. The resulting initial pressure drop of coated filter media is shown in table 3. Even with rather thick layers and a coverage of more than 90% of the surface area the pressure drop rises from 0.4 kPa to only about 1 kPa for an air flow of $150 \text{ m}^3/(\text{m}^2 \text{ h})$.

This shows that the membranes themselves are porous, a fact that could be expected from the conditions of hydrolysis and condensation. The specific

Table 3

Initial pressure drop of membrane coated glass fiber fleeces for an air flow of $150 \text{ m}^3/(\text{m}^2 \text{ h})$

No.	Corresponds to		Initial pressure drop (kPa)
	Experiment no. in table 2	Fig.	
1	–	1b	0.4
2	–	3a	0.45
3	–	3b	0.45
4	1	–	0.4
5	3	–	1.2
6	4	4a	0.6
7	2	4b	0.8
8	–	4c	0.7
9	6	4d	1.0

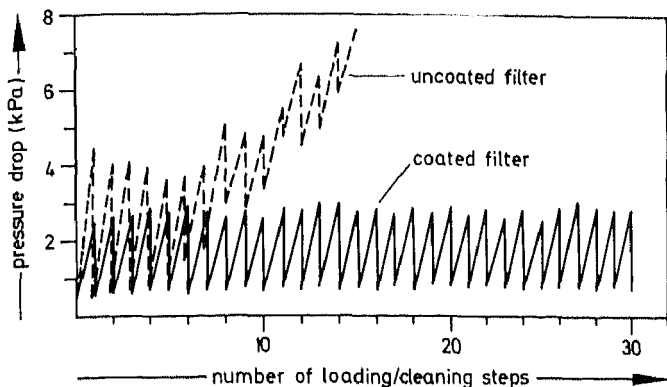


Fig. 6. Changes of pressure drop after loading (upper points) and cleaning (lower points) of a coated and uncoated filter.

surface areas of the thick membranes (5–10 μm) amount to 200–300 m^2/g , the mean pore diameters are below 2.5 nm. Since it was difficult to separate the membrane from the support, the determination of the specific surface area was carried out with the coated specimen. The determination of specific surface areas and pore diameters of thin membranes failed, since the amount of membrane material was too small in this case. In a laboratory test related to practical use the cleaning behaviour of a membrane coated filter was tested in comparison to that of an original filter. The filter was loaded and regenerated about 30 times under well defined conditions and the pressure drop was measured after every loading and cleaning step (fig. 6).

The uncoated filter shows the typical behaviour of a deep bed filter with continuously increasing pressure drop. This increase indicates the irreversible clogging of the filter volume. On the contrary, the coated filter shows only a small increase during the first steps, then reaching a constant value after every loading/cleaning cycle. The dust is retained at the membrane, the volume of the filter is free of dust. Supplementary experiments made sure that the mechanical stability of those membranes was high enough to bear even pressure shocks up to more than 5 bar from the uncoated side during the cleaning step, showing the excellent adhesion of the membranes to the support.

4. Conclusion

The investigations showed that siliceous membranes can be reacted onto the surface of porous supports using the sol-gel method. Various preparation techniques are possible, the reaction via the vapour phase is the most useful. The membranes, which can also be prepared continuously, fulfill the preset requirements. The general possibilities of the sol-gel method, like the tailoring of specific properties by variation of the reacting system and the reaction conditions, are fully valid for the described membrane preparations.

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Discussion

This paper opens a new sol-gel field which has to compete with plastic (organic) membranes and glass hollow fibers produced by leaching or otherwise produced porous glass.

In the intensive discussion A. Kaiser answered a question by *J.D. Mackenzie* concerning practical fields of use, giving one example, that of the filtering of dust from air (clean room technology).

C. Schüler asked for the pore size of the films and how to alter them. The answer was that the pore size of the thicker membranes was determined to be ≤ 2.5 nm. Variations can be introduced by changing the parameters of production given in the table, especially the kind of catalysts.

D.R. Uhlmann recalled the similarity to organic polymer membranes where the immiscible liquid approach is similar to the interfacial polymerization (IFP). So the characteristics of the coatings are influenced. He asked for such effects. *A. Kaiser* answered that difficulties occurred because the reaction had to be run very rapidly and the support had to be placed in the interphase before adding the catalyst. This sometimes leads to a disturbance in the system and effects the properties of the coatings. Experiments with reversed order had been performed too, but they were stopped for experimental reasons. The effect on membrane characteristics, especially with respect to that item, was not examined in detail.

H. Schmidt answered that, as a function of the chemical nature of the

reacting system, in the liquid-liquid interface oligomeric compounds are produced which at low reaction rates have time to diffuse into the aqueous phase and form polymers there. Because of that the choice of suitable reaction conditions is a prerequisite of proper membrane preparation.