

# ULTRASTRUCTURE PROCESSING OF ADVANCED CERAMICS

EDITED BY

JOHN D. MACKENZIE  
*University of California—Los Angeles*

DONALD R. ULRICH  
*Air Force Office of Scientific Research,  
Washington, D.C.*

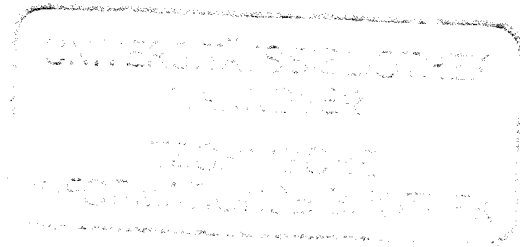


WILEY

A WILEY-INTERSCIENCE PUBLICATION

**John Wiley & Sons**

New York   Chichester   Brisbane   Toronto   Singapore



# DEVELOPMENT OF ORGANIC-INORGANIC HARD COATINGS BY THE SOL-GEL PROCESS

H. SCHMIDT, B. SEIFERLING, G. PHILIPP,  
and K. DEICHMANN

Fraunhofer-Institut für Silicatforschung, Würzburg,  
Federal Republic of Germany

## 1. INTRODUCTION

Mechanical protection of "precious" but soft surfaces is still a problem for many substrates. Many materials with good properties with respect to the main application fail by reason of their soft surface. Thus, for instance, transparent synthetic polymers that can be prepared with optical quality can only be used for a few applications, since the optical quality decreases rapidly with scratched surfaces. Even simple plastic materials for household purposes suffer from their non-scratch-resistant surface and are only used for low-value articles. But even in cases where the synthetic polymer is doubtlessly advantageous compared to inorganic materials such as glass (e.g., from security reasons), low mechanical surface strength often prevents a wide application. Many efforts are made in order to overcome the described disadvantages. Thus, scratch-resistant polymers, such as CR 39, a polyallylethercarbonate, were developed for eyeglass lenses. But even this polymer is far away from the surface hardness of inorganic glasses. Recently, the developments of scratch-resistant coatings have reached a level to be widely applied. Most of these coatings are based on polyorganosiloxanes (modified silicones)<sup>1</sup> and their high scratch resistance can be attributed to the

"inorganic"  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  backbone. The systems in the form to be applied are "living" systems. They are often tricky to handle as well as being sensitive to moisture, temperature, and time, since they are sol-gel-derived, with no organic cross-link-containing precondensates. Thicker layers ( $\geq 20 \mu\text{m}$ ) are difficult to be obtained. The question arises as to how these disadvantages can be overcome by synthesis of polymers based on inorganic networks. Therefore, the use of network formers different from silica also seems to be of interest. For suitable processing and mechanical properties (e.g., shrinkage and modulus of elasticity), an additional organic polymeric network should be of benefit. A group of materials with a hopeful application potential for the described purpose are inorganic-organic polymers, according to various authors.<sup>2-7</sup> Therefore, the sol-gel process<sup>8-11</sup> was proved to be a suitable method, since it allows us to synthesize inorganic networks at low temperatures. To densify pure inorganic networks, fairly high temperatures are also required, but the introduction of organic components can reduce the network connectivity in a way such that dense materials can be achieved by low-temperature processing.<sup>12</sup> From Schmidt et al.<sup>7</sup> it was known that using the system  $\text{Si}(\text{OR})_4/\text{Ti}(\text{OR})_4/\text{CH}_3\text{OCO}(\text{CH}_3)\text{C}=\text{CH}_2/(\text{RO})_3\text{Si}(\text{CH}_2)_2\text{OCO}(\text{CH}_3)\text{C}=\text{CH}_2/(\text{RO})_3\text{Si}(\text{CH}_2)_3\text{OCH}_2\text{CH}-\text{CH}_2\text{O}$  (I) as starting compounds, solid polymers can be synthesized with hard surfaces. In these polymers, the epoxide was reacted to a glycol group, and the methacrylates were polymerized by radical polymerization. In order to perform homogeneous reaction the "CCC" condensation principle was developed.<sup>6</sup>

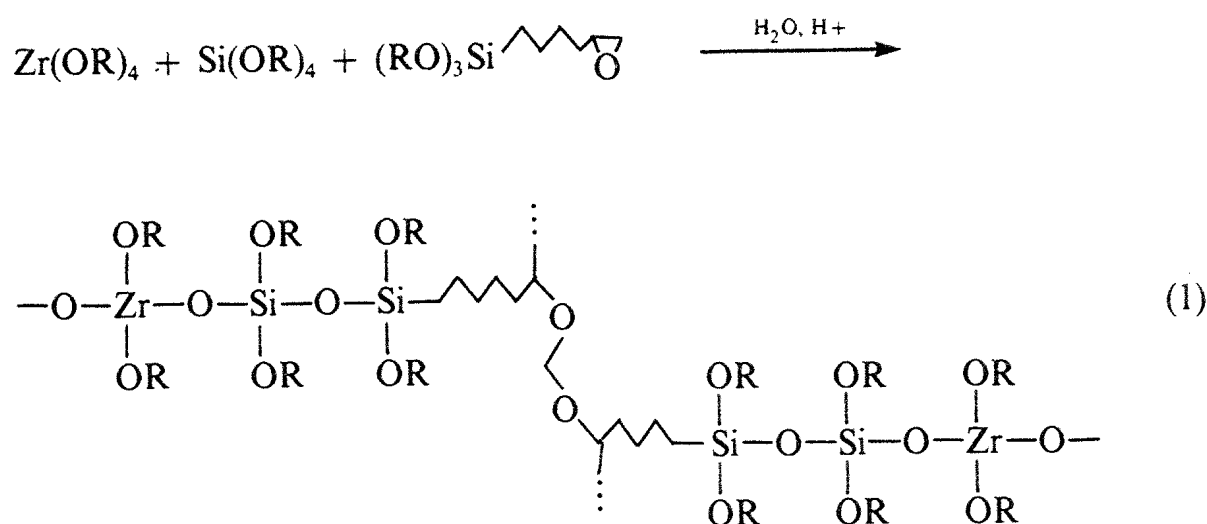
Up to now, CR 39 has been the most common polymeric material for eyeglasses. It is fairly scratch resistant, polymerizable in sufficient optical quality, and of high chemical and mechanical stability. In previous work,<sup>6,13</sup> it was shown that with epoxysilane (I) one could synthesize Si, Ti, Al, and Zr polymers that could be used for hard coatings. Based on this, an optimization of these materials was carried out and a coating procedure for CR 39 lenses was developed. For material production the chemical engineering step for the sol-gel process was carried out for industrial production.

## 2. EXPERIMENTAL DEVELOPMENTS AND RESULTS

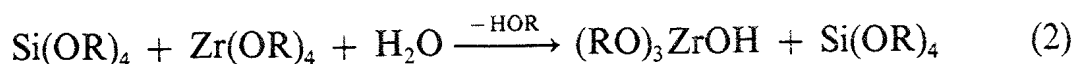
### 2.1. Chemistry

A synthesis process was developed on the laboratory scale first. Therefore, the starting compounds tetramethylsilicate ( $\text{Si}(\text{OMe})_4$ ), one of the alkoxides of Zr, Al, or Ti, and the epoxysilane (I) were mixed at room temperature; also, silica gel, loaded with the adequate amount of water necessary to perform one-sixteenth to three-sixteenths of the hydrolysis of all present OR groups, and 0.1 N HCl were added. The mixture was stirred for 2 hr at room temperature and then stored. During this procedure, condensation and epoxide polymerization

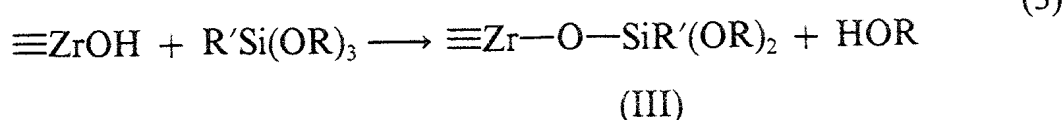
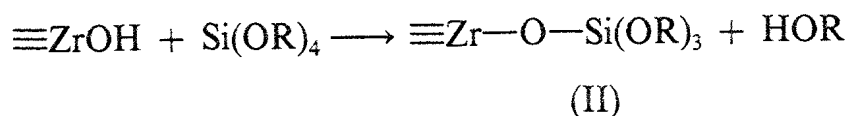
partially took place as shown in Eq. (1):



This prepolymer is still a low viscous liquid and can be diluted, if necessary. Suitable solvents are butanol, ethylacetate, and similar organic solvents. The epoxide polymerization is catalyzed by the alkoxides.<sup>13</sup> The degree of epoxide group consumption reaches values as high as 80%. The analysis was carried out according to ref. 14. In contrast to the water addition via silica and the CCC method, the addition of plain water to the precursors leads to the precipitation of the reactive alkoxides such as Ti or Zr, and no coating material can be received. The silica donates water so slowly and homogeneously that no precipitation takes place. It can be assumed that in a mixed alkoxide system including  $\text{Si(OR)}_4$ , the hydrolysis of the reactive components takes place according to Eq. (2):



but as a next step, and because of lack of water in the system, the  $\equiv\text{ZrOH}$  group, for example, reacts with any  $\equiv\text{MeOR}$  group it can find, as indicated in Eq. (3):



Experiments show that after only one-sixteenth hydrolysis of the total amount of OR groups in systems based on (I),  $\text{Si(OR)}_4$ , and reactive alkoxides such as  $\text{Zr(OR)}_4$  by CCC or the silica method, the fully stoichiometric amount of water can be added without precipitation or visible inhomogeneities being observed: Zr now must be incorporated in the prepolymer network including all present

components so that no precipitation of zirconium hydroxide by further hydrolysis can take place.

The prepolymers derived according to Eq. (1) (mol % (I) = 50–70;  $\text{Si}(\text{OR})_4 = 10\text{--}30$ ;  $\text{Me}(\text{OR})_4 = 10\text{--}20$ ) can be stored for months without changing their viscosity (capillary viscosimeter).

## 2.2. Coating

For preparation of the coating material, the rest of the water necessary for complete hydrolysis has to be added to the prepolymer. For purposes where no special high quality has to be achieved, the system can be applied as is. For coating of CR 39 lenses, the coating material has to be diluted. Fifty weight percent of butanol as solvent was found to give high-quality optical coatings; 0.2 wt % of a flowing agent has to be added, too. Then, a shelf life of 10 hr can be guaranteed (3% viscosity increase only).

Different coating techniques for CR 39 lenses were tested: Dip coating leads to high-quality coatings but is very sensitive to vibrations, temperature changes, and solvent evaporations. Therefore, a spin-on process with about 1200 rpm was chosen and proved to be satisfying (see Fig. 1).

The coating has to be performed under dust-free conditions (clean-room technology) in order to avoid dust particles that contaminate the lens surfaces. A 4–5- $\mu\text{m}$ -thick coating can be achieved by a single coating step. For sufficient scratch resistance, a coating thickness of  $\geq 10\ \mu\text{m}$  is useful (for data see Table 1).

## 2.3. Drying and Curing

Drying to a nonadhesive surface occurs at room temperature during spinning within 1 min after the coating liquid supply stops. The surface then is still soft.

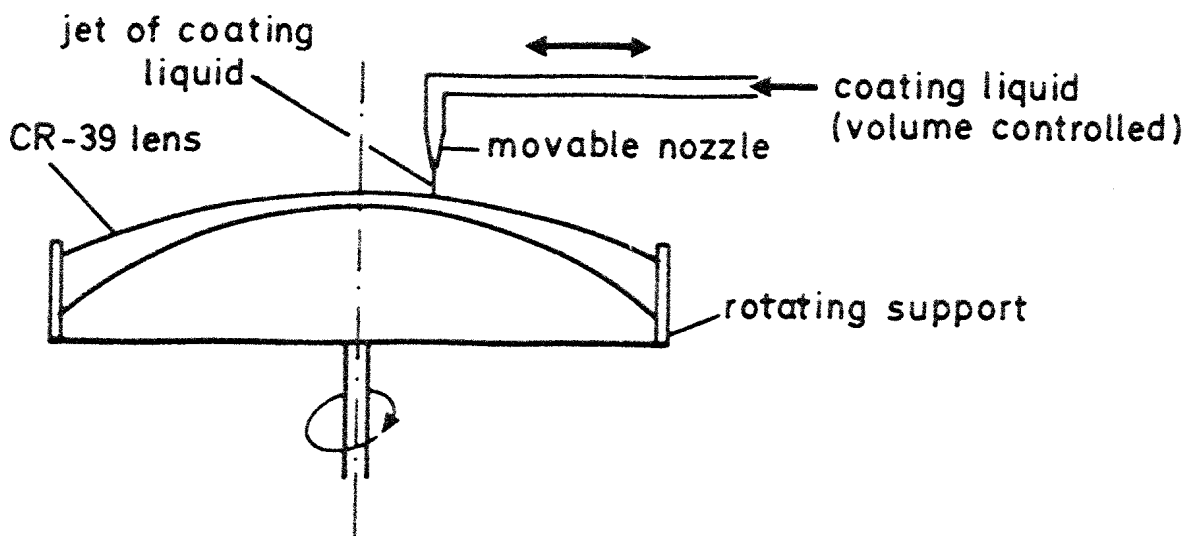


Figure 1. Scheme of the spin-on coating procedure of CR 39 eyeglass lenses.

TABLE 1. Scratch and Abrading Tests of Different Coatings (Composition (mol %): MeO<sub>2</sub>, 20; Epoxysilane, 50; SiO<sub>2</sub>, 30)

Test	Coatings and Polymers				
	CR 39 (Uncoated)	PMMA (Uncoated)	Coating 1 (Zr-containing)	Coating 2 (Ti-containing)	Coating 3 (Al-containing)
a (load in g)	1-2	< 1	10	20-30	50
b (haze in %) (200 rev.)	12-13	> 20	---	1.5	---
c (haze in %)	4 <sup>a</sup>	---	---	1.2	---
	15 <sup>b</sup>	---	---	6	---

<sup>a</sup>Diamond powder.

<sup>b</sup>Boron carbide powder.

Curing to a hard surface occurs at 120°C within 15 min (thermal or infrared). Thicker coatings can be achieved by a multiple-step coating where only a short drying period (some minutes at 120°C) has to be carried out between the coating steps. The 15-min curing can be done after the last coating step.

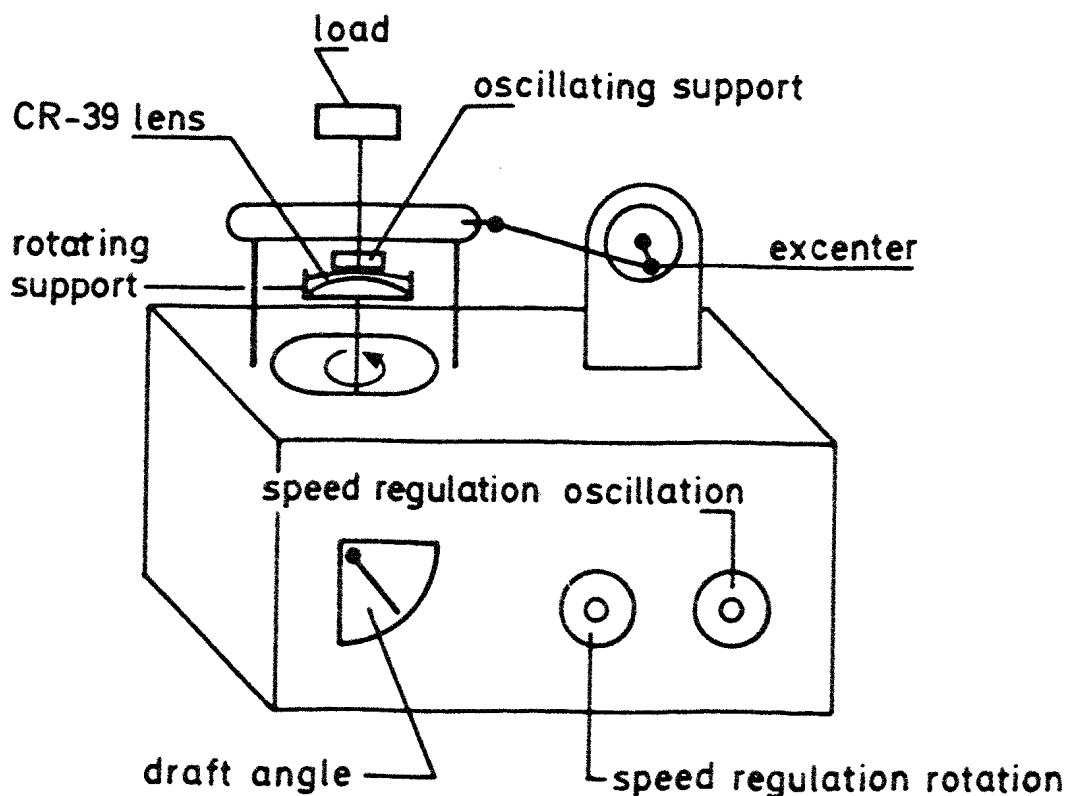
## 2.4. Adhesion Promotion

In order to achieve a good adhesion of the coating to the CR 39 surface, the use of an adhesion promoter has to be recommended.  $\gamma$ -aminopropyltriethoxysilane was found to be a good adhesion promoter (5 wt % in butanolic solution; treatment of the lenses before coating).

## 3. PROPERTIES OF THE COATING

### 3.1. Scratch Resistance

The data obtained by surface hardness tests depend strongly on the applied test. Test conditions that are representative for the special application have to be found or developed. For the lens surface-hardness determination, three different



**Figure 2.** Scheme of the special abrasion-testing device. The lens is rotated by a rotating support and loaded by a felt oscillating support connected to an excenter disk; abrasive powder suspension is added before starting; oscillation and rotation speed can be varied.

tests were chosen (two of them had to be developed):

1. The diamond scratch test; this test should simulate a scratch caused, for example, by a sand particle to be rubbed over the surface during cleaning. Therefore, a vickers diamond was scratched over the surface with a well-defined load. The process is observed by microscope, and the load at which the first scratch becomes visible represents the scratch-resistance number (test a).
2. The Taber abrader test was used as a standardized method for comparison (test b); haze was measured (percentage of scattered light compared to the nonscratched surface).
3. A special abrasive test simulating extended cleaning under "dirty," (i.e. dust-contaminated) conditions (test c, Fig. 2). This test allows us to use different abrasive powders, thus simulating different forms or hardness of abrasive particles (haze according to test b).

The results of different tests and coatings are given in Table 1.

The test shows clearly that the coatings improve the surface properties remarkably, as compared to the uncoated materials.

In addition to this, a haze test was carried out on a float glass plate under the conditions of Table 1 (200 revolutions). Coating 2 shows 1.5% haze, glass shows 1.2% haze.

**TABLE 2. Summary of Important Tests of Coated Eyeglass Lenses**

Test	Result
3-min ultrasonic treatment (10 wt % tartratic acid in water)	Coating unaffected
Antireflective coating	To be applied without problems
Coloring by dye diffusion	Without problems
3-min ultrasonic treatment in 0.1 N NaOH	Minor cracks on lab products around coating defects only
Temperature change in water baths (+90 to +15°C), 5 cycles	Coating unaffected
Temperature change in lab air (+80 to -20°C)	Coating unaffected
16-hr physiological NaCl solution, room temperature	Coating unaffected
Xenotest (ultraviolet lamp 180 klux)	> 80 hr, unaffected (with appropriate ultraviolet absorber)
Adhesion	Cross-cut test before (5) and after tape test (4.5-5)



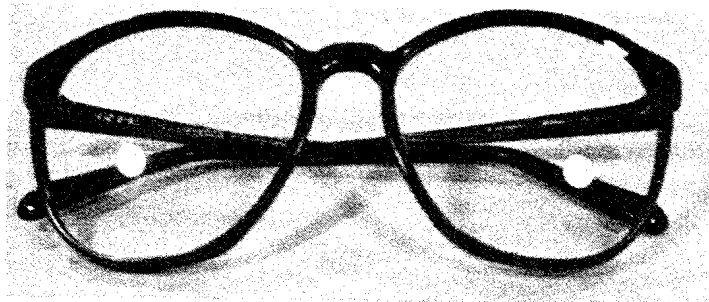


Figure 3. Photograph of a mounted eyeglass with scratch-resistant coated glasses showing clear, transparent lenses.

### 3.2. Other Properties

A series of tests was performed to meet the German standards for polymeric eyeglass lenses. Table 2 presents a summary of a survey on the most important test results. One can point out that the new coating material leads to remarkable improvement as compared to common CR 39 plastic eyeglass lenses. Figure 3 shows a photograph of mounted eyeglasses with coated lenses.

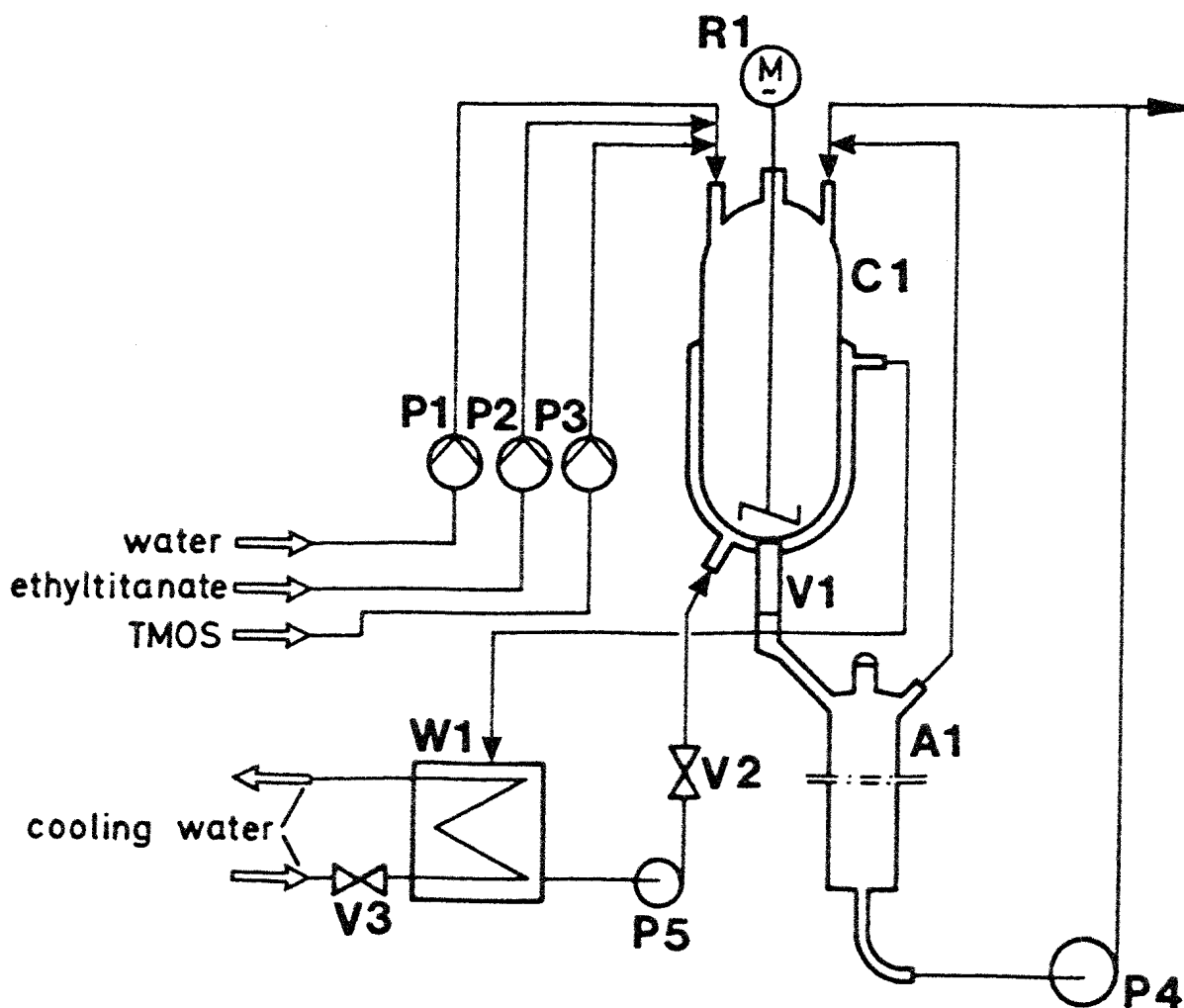


Figure 4. Flow sheet of the industrial-scale production of the scratch-resistant coating material: A1, filtering apparatus; C1, reactor; P1-P3, diaphragm metering pumps; P4, magnetic centrifugal pump; P5, centrifugal pump; R1, stirrer; V1, drain valve; V2, primary-cooling-circle water valve; V3, secondary-cooling-circle water valve; TMOS, tetramethylorthosilicate.

#### 4. SCALING UP

For industrial production, a production line was built up, as shown in Fig. 4.

The chemical reaction takes place in the main reactor (C 1), which can be cooled during the reaction. The reactor, containing the starting compound and abrasion-resistant silica gel pellets for the reaction water supply, is stirred during the one-sixteenth hydrolysis. After reaction, the product is filtered in A1 and pumped into the storage tank. The precondensate has to be stored in a close tank. The storage time is not limited. For coating, the appropriate concentration of water is added to the needed amount of the precondensate; then the mixture is stirred at room temperature for half an hour and is ready for a 10 hr period for coating.

#### 5. CONCLUSIONS

The development shows that the sol-gel process enables one to synthesize special organic-inorganic polymers, since the inorganic network can be synthesized at temperatures low enough for organics to survive. In the described case, properties of the inorganic components as well as of the organic components were combined for the desired application. The organic polymerization leads to a sufficient flexibility of the network to apply thick coatings (10–20  $\mu\text{m}$ ) without the necessity of a proper  $\alpha$  (thermal expansion coefficient) matching. Moreover, it leads to a prepolymer that can be cured without drastic shrinkage (5–7% only) to a dense solid. The inorganic network leads to a high scratch resistance and to the possibility of quick thermal curing by three-dimensional polycondensation-based cross-linking by heat. It shows further that the sol-gel technique could be scaled up for industrial use and that new materials can be synthesized with good payback prospects.

#### ACKNOWLEDGMENTS

The authors wish to thank the Rupp and Hubrach Company and the Minister for Research and Technology of the Federal Republic of Germany for the financial support. They further thank Mr. Ondratschek and Mr. Hofmann from the Fraunhofer Institute for Automation and Production Technology in Stuttgart for their experimental and technical assistance.

#### REFERENCES

1. S. H. Schroeter and D. R. Olson, Abrasion Resistant Silicone Coated Polycarbonate Article, U.S. patent PCT Int. Appl. 8,000,940, May 15, 1980.
2. K. A. Andrianov, *Organic Silicon Compounds*, State Scientific Publishing House for Chemical Literature, Moscow (1955).

3. K. A. Andrianov and A. A. Zhdanov, Synthesis of New Polymers with Inorganic Chains of Molecules, *J. Polym. Sci.*, **XXX**, (1958).
4. G. L. Wilkes, B. Orler, and H.-H. Huang, Ceramers, *Am. Chem. Soc. Div. Polym. Chem.*, **26**, (1985).
5. H. Schmidt, Organically Modified Silicates by the Sol-Gel Process, *Mater. Res. Soc. Symp. Proc.*, **32**, (1984).
6. H. Schmidt and B. Seiferling, Chemistry and Applications of Inorganic-Organic Polymers, *Mater. Res. Soc. Symp. Proc.*, **73**, (1986).
7. H. Schmidt, G. Philipp, and Ch. F. Kreiner, 'Kieselsäureheteropolykondensate und deren Verwendung für optische Linsen, insbesondere Kontaktlinsen, EP 0 078 548, November 4, 1982.
8. H. Dislich, Neue Wege zu Mehrkomponentenoxidgläsern, *Angew. Chem.*, **83**, (1971).
9. R. Roy, Gel Route to Homogeneous Glass Preparation, *J. Am. Ceram. Soc.*, **52**, (1969).
10. S. Sakka and K. Kamiya, Glasses from Metal Alcoholates, *J. Non-Cryst. Solids*, **43**, (1980).
11. J. D. Mackenzie, Glasses from Melts and Glasses from Gels, a Comparison, *J. Non-Cryst. Solids*, **48**, (1981).
12. H. Schmidt, H. Scholze, and G. Tünker, Hot Melt Adhesives for Glass Containers by the Sol-Gel Process, *J. Non-Cryst. Solids*, **80**, (1986).
13. G. Philipp and H. Schmidt, The Reactivity of  $\text{TiO}_2$  and  $\text{ZrO}_2$  in Organically Modified Silicates, *J. Non-Cryst. Solids*, **82**, (1986).
14. W. Glaubitt, Quantitative Bestimmung von Epoxid- und Glycolgruppen in organisch modifizierten Silicaten, Diploma thesis, University of Würzburg (1986).