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Paper 31

SELF-ASSEMBLING FLUORINE-CONTAINING NANOCOMPOSITE COATINGS BY SOL-GEL TECHNIQUES

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Self-Assembling Fluorine-Containing Nanocomposite Coatings by Sol-Gel Techniques

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The sol-gel process opens the possibility of combining inorganic and organic units on a molecular or nano-size level. Key factor is the incorporation of organic groupings linked to the inorganic backbone, formed by hydrolysis and condensation, e.g. starting from alkoxides. The organic groupings can play the role of network modifiers (alkyl, aryl, ...), the role of a second type of network formers (vinyl, methacryl, epoxy, ...) or the role of the carrier of special functions compared to purely inorganic sol-gel-derived materials. The densification temperatures of these composites are drastically decreased in comparison to pure inorganic sol-gel materials, and organics can be incorporated, in general, without being decomposed.

For the preparation of multicomponent systems, especially with groupings of different polarity, it is necessary to develop a very special synthesis technique. For example, if compounds with low molar refraction for obtaining low refractive indices are used, as it is the case with fluorinated hydrocarbons, phase separation takes place and turbid systems are produced, even if the fluorinated groupings are bound to hydrolysable and condensable silanes.

A very special synthesis route has been developed for obtaining highly transparent systems with low refractive indices ≥ 1.39. Measurements of the surface free energy of these systems show low values up to 19 mJ/m². The surprising fact of these systems when applied as coating is that the surface free energy of about 19 mJ/m² does not change up to $\equiv Si(CH_2)_2(CF_2)_5CF_3$ contents of as low as 1 - 6 mole%. Investigations of the coating by ESCA depth profiling show that fluorine is enriched at the surface and a gradient is formed. The principle of the enrichment of fluorinated side-chains by self-assembling is successfully proven for different inorganic-organic nanocomposite materials, suitable for the coating (dip, spin, spray, roller coating) of (transparent) polymers and for coatings with a high temperature stability ≤ 350 °C for metals and glass. Advantages of this type of materials in comparison to coatings based on perfluorinated polymers are the transparency of the coatings, the high scratch and abrasion resistance and the avoidance of adhesion problems by the self-assembled surface-enriched fluorinated chains. Because of the good adhesion of the transparent coatings, the environmental stability and achieved low surface free energies, a wide range of applications of this type of coatings in the field of antiadhesion/antisoiling is of interest.

- Incorporation of small amounts of perfluorinated chains in inorganic- organic nanocomposites leads to low surface energies similar to PTFE- surfaces
- Transparency
- Mechanical properties similar to glass surfaces
- Environmental stability
- Cheap according to conventional coating technologies
- Many applications possible for antisoiling properties

Idea

- Incorporation of perfluoroalkylsilanes into transparent sol-gel-derived inorganic-organic nanocomposites

⟹ three functions of the coating material:

I low surface free energy by an enrichment of fluorinated chains at the surface to achieve low surface-free energies
II high scratch and abrasion resistance by the inorganic SiO_2 network
III good adhesion

⟹ advantages:

- „perfluorinated surface": low energy
- low amount of fluorine: recycling possible
- one step coating: smart processing

Low Energy Coatings

- Glass surfaces are high energy surfaces because of high concentration of OH groups

  - high polar part of the surface energy (low contact angle for water)
  - high stability of adsorbed layers (hydrophobic behavior in practical use)

➔ what is needed:
- better means for manipulation of the surface properties
- maintainance of transparency and sufficient mechanical properties

-reduction of wettability and thereby of the free surface energy leads to decreased stability of the adsorbed layers

- perfluorinated polymers show low wettability for polar and unpolar liquids and thereby very low surface free energies

  - low adhesion
  - low transparency
  - "soft" surface

Low Refractive Index Coatings

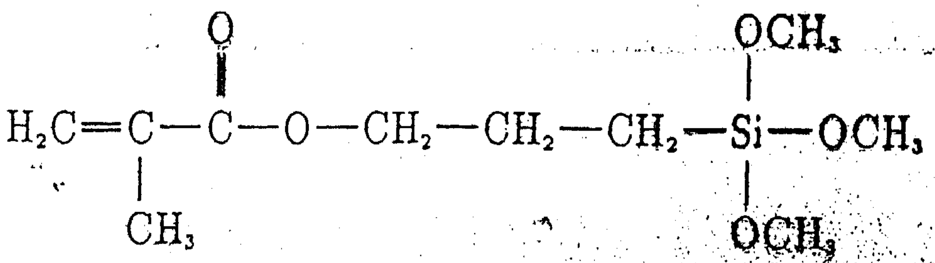
Objective:
- transparent coating, ≈ 5µm
- good adhesion and scratch resistance
- wet climate stability
- easy processable (dip-, spincoting)
- index of refraction ≤ 1.4

Idea: incorporation of fluorine in an Sol-Gel derived inorganic organic composite because of low molar refraction

Owens(1965): coating based on $CH_3Si(OR)_3$

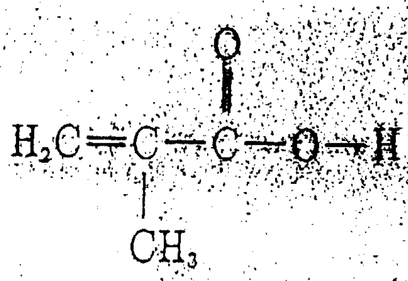
$n_D = 1{,}418$

starting materials



MPTS

$Zr(OPr)_4$ **Zr**



MAS

$CF_3CH_2CH_2Si(CH_3)(OCH_3)_2$ **TPS**

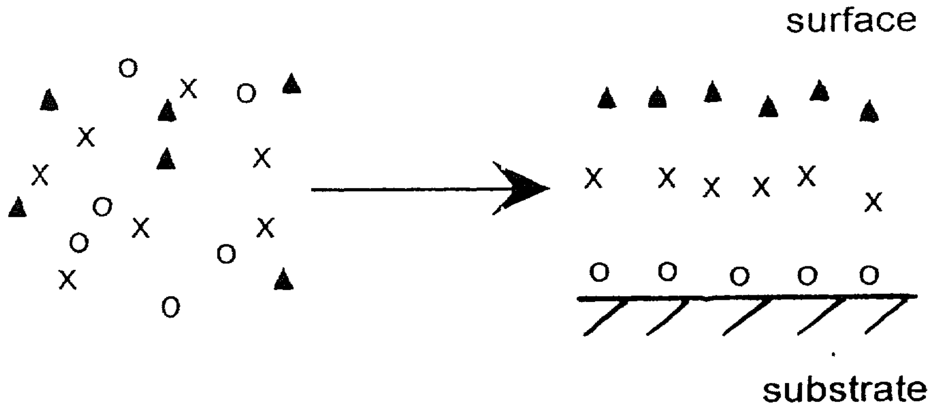
$CF_3(CF_2)_6CH_2CH_2Si(OCH_2CH_3)_3$ **FTS**

$CF_3(CF_2)_8CH_2CH_2Si(OCH_2CH_3)_3$ **FTS2**

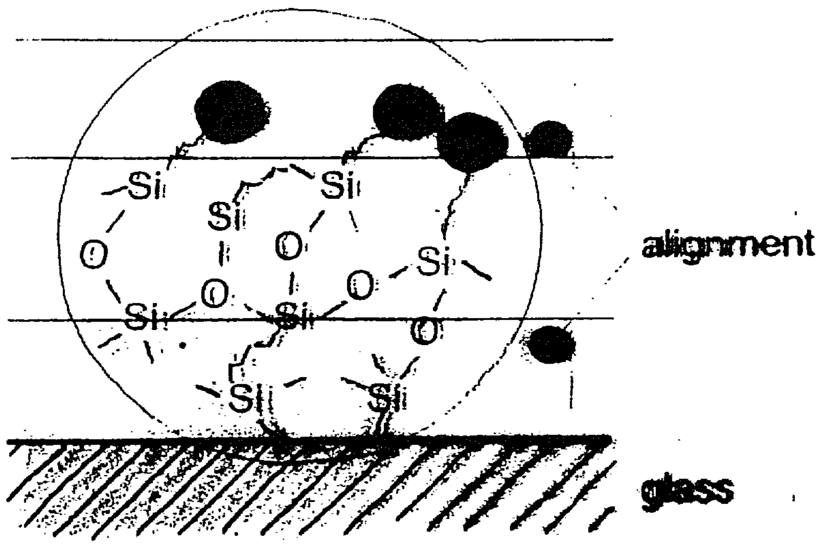
Material Properties

- transparent
- adhesion: cross cut-/ tape test 0/1
- wet climate: adhesion uneffected
- UV test: no optical change

- thermodynamic approach: minimisation of the energy of the coating by enrichment of fluorinated chains at the coating/air interface during curing



- low energy by perfluorinated side chains ($CF_3(CF_2)_5(CH_2)_2Si(OR)_3$, FTS)



Properties

- easy processable (dip- spincoating, thermal curing)

- transparent

- adhesion (cross cut/tape test): 0/1

- wet climate stability (14 d, DIN 50017): adhesion uneffected

- scratch resistance (modified Erichsen Test): 3-4g;
  glass < 1g

☐ Material Properties

- <u>Adhesion:</u>
  method: crosscut/ tape test (DIN 53191, ASTM D 3359)
  → between 0 and 1 (very good adhesion) for coatings containing less than 3 Mol% of FTS

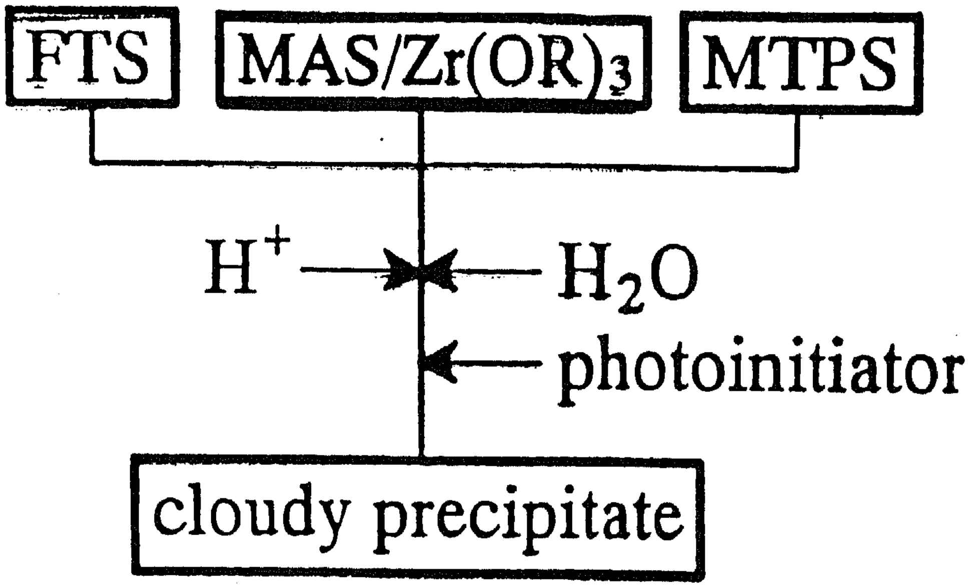
- <u>Wet climate test:</u>
  14 d DIN 50017
  → adhesion uneffected

- <u>UV- stability:</u>
  14 d DIN 53384 (continous UV- treatment, cycles of 1 h rain, 5 h 50°C/ 10% humidity)
  → no yellowing, adhesion uneffected, decrease of contact angles (≈ 5°)

- <u>Abrasion resistance:</u>
  method: DIN 53247, measurement of scattering light after 100 cycles Taber Abrader
  → scattering light loss ≈ 1,5% (glass ≈ 1%, polycarbonate ≈ 30%)

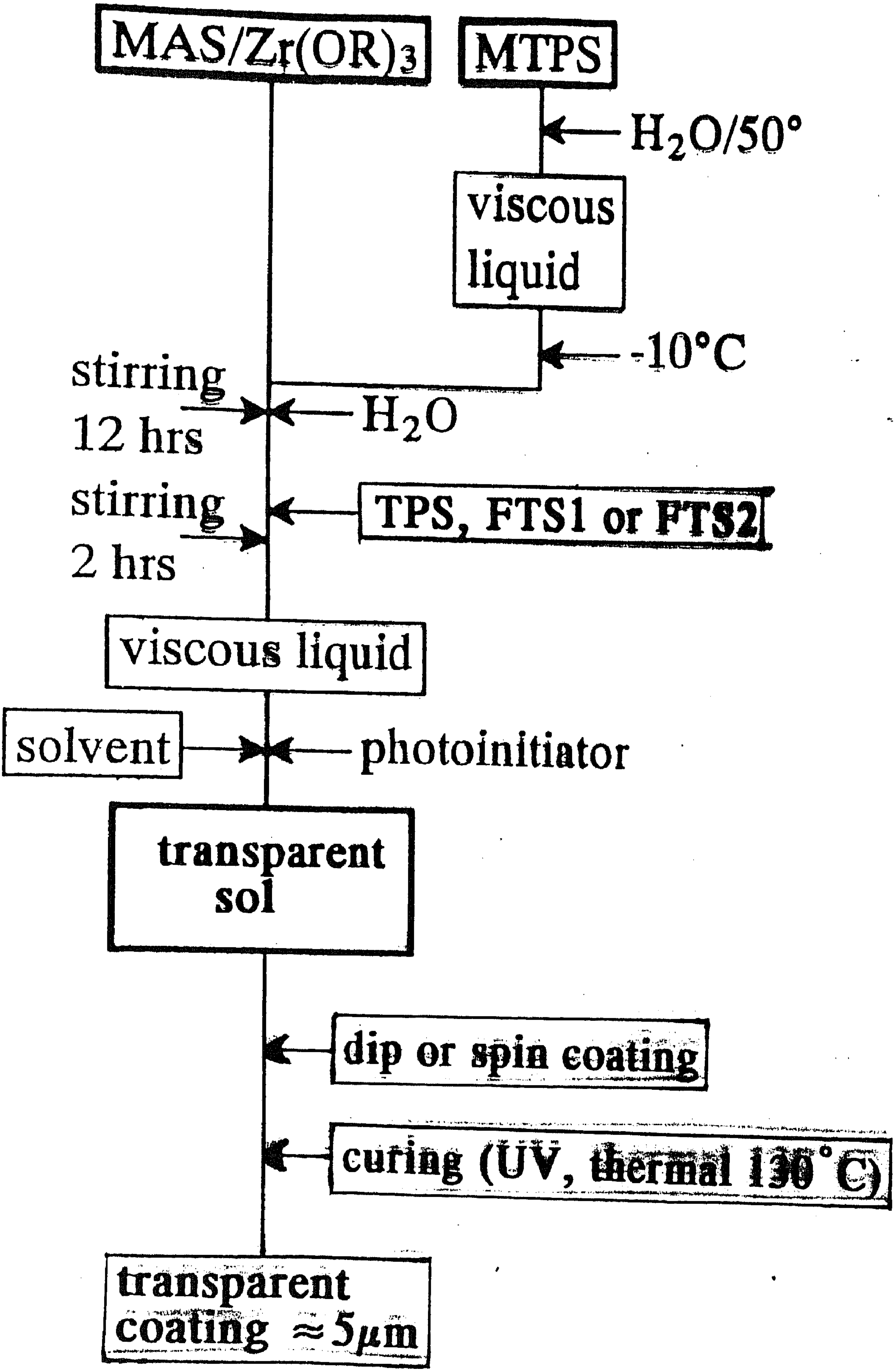
- <u>Soil repellency:</u>
  method: substrates are sprayed by a defined amount of "model soil" (a suspension of aerosil and motor oil in water)
  → look at Fig. 1

Synthesis



Optimisation:

- **Hydrolysis in steps (rel. reaction rates)**
- **reaction control (KF- titration, ^{29}Si- NMR)**



MAS/Zr(OR)3
MTPS
H2O/50°
viscous liquid
-10°C
stirring 12 hrs
H2O
stirring 2 hrs
TPS, FTS1 or FTS2
viscous liquid
solvent
photoinitiator
transparent sol
dip or spin coating
curing (UV, thermal 130°C)
transparent coating ≈5μm

Construction principles of inorganic-organic nanocomposites

Sol-Gel Process

inorganic network
- molekular
- small particles
- combinations

organic groups linked to inorganic units via

σ-, coordinative- or adsorptive-bonds

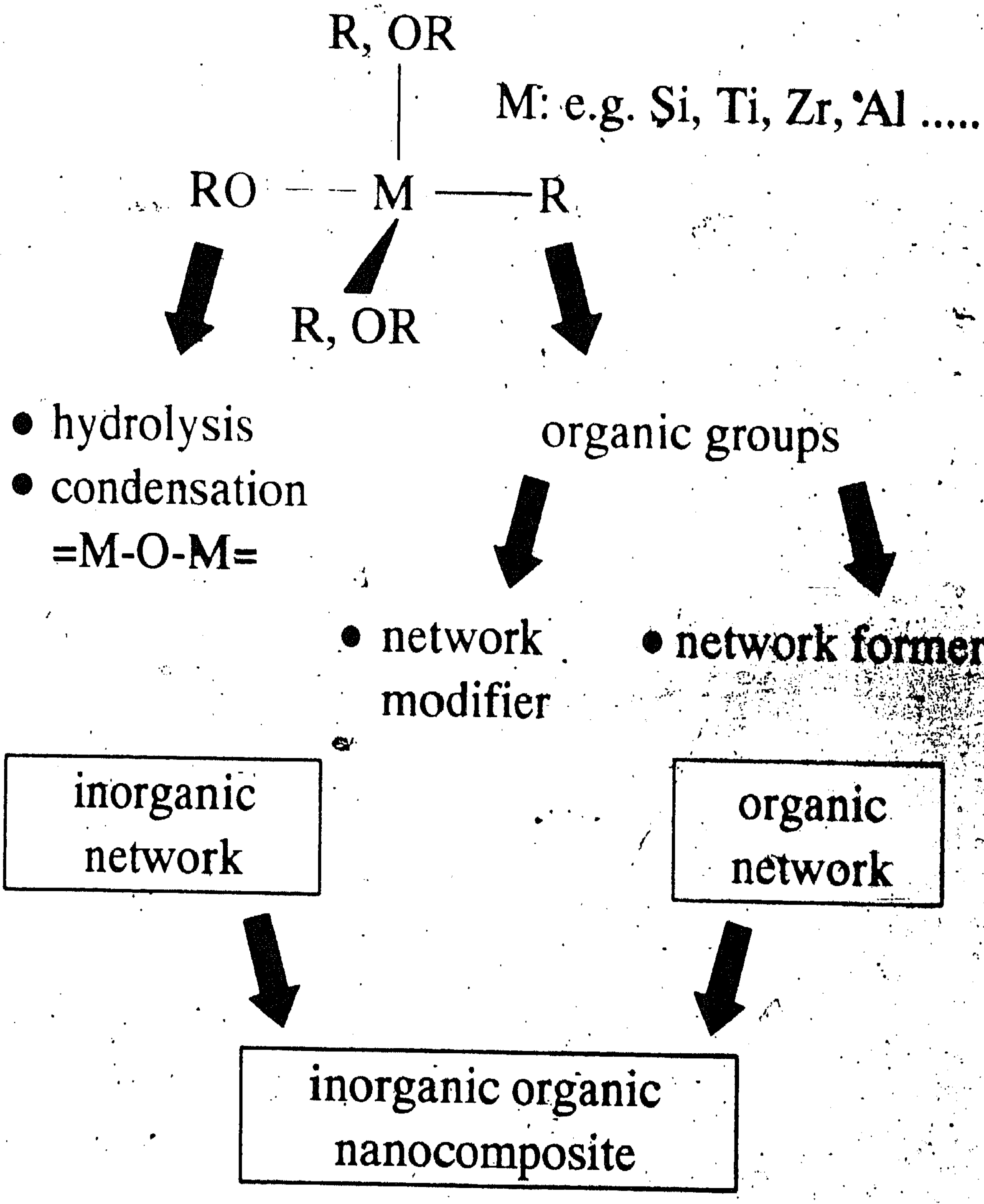
→ variety of functions:
- organic network modifiers
- organic network formers

→ **inorganic-organic or molecular nanocomposites**

Properties

optical	mechanical	chemical	electrical
- transparent	- adhesion	- UV stability	- dielectric
- passive	- hardness	- tailored surface properties	- ion conductivity
- active (NLO)	- scratch & abrasion resistant		
- tailored n_D, v_D			

14.


R, OR
M: e.g. Si, Ti, Zr, Al .....
RO
M
R
R, OR
• hydrolysis
• condensation
=M-O-M=
organic groups
• network modifier
• network former
inorganic network
organic network
inorganic organic nanocomposite

Sol-Gel-Prozeß

Hydrolyse:

$M\text{-}OR + H_2O \longrightarrow MOH + ROH$

Kondensation:

$M\text{-}OH + HO\text{-}M \longrightarrow M\text{-}O\text{-}M + H_2O$

$M\text{-}OR + HO\text{-}M \longrightarrow M\text{-}O\text{-}M + ROH$

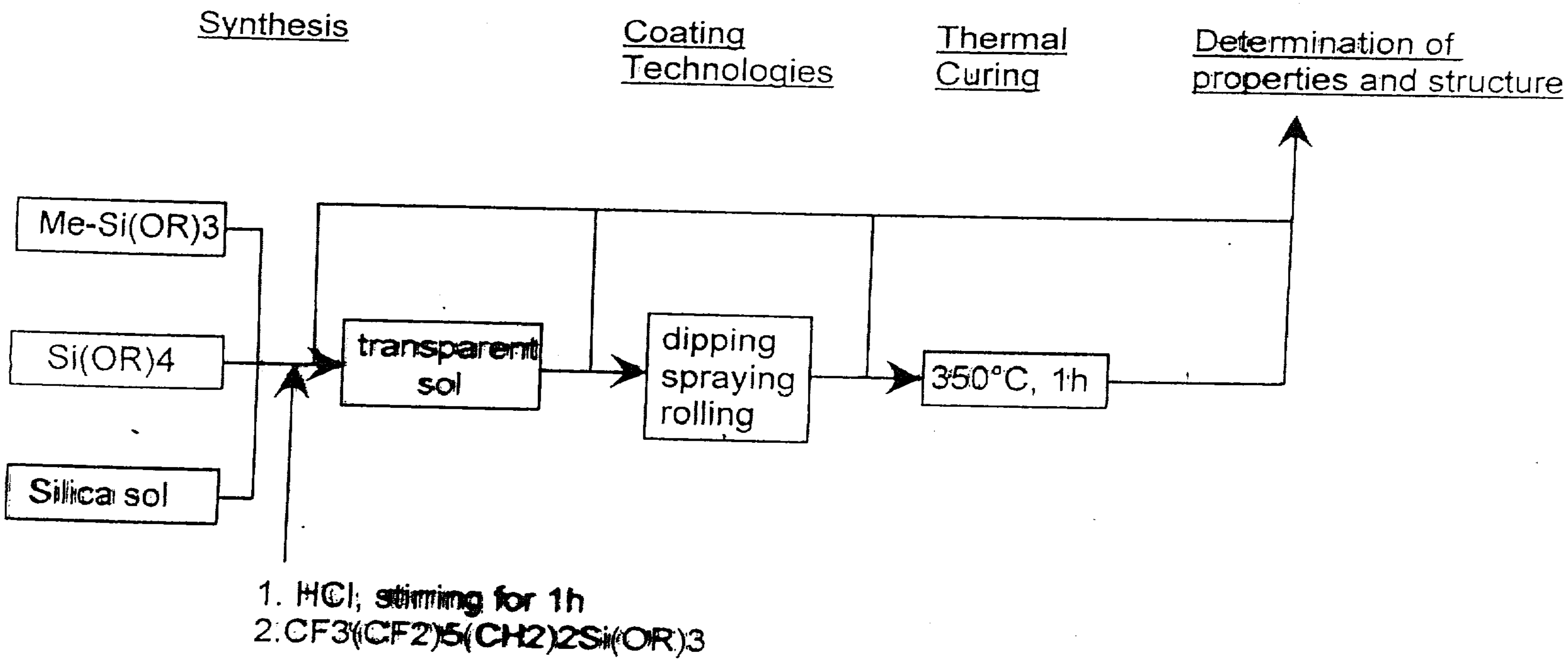
M z. B. Si, Zr, Al, Ti ...;

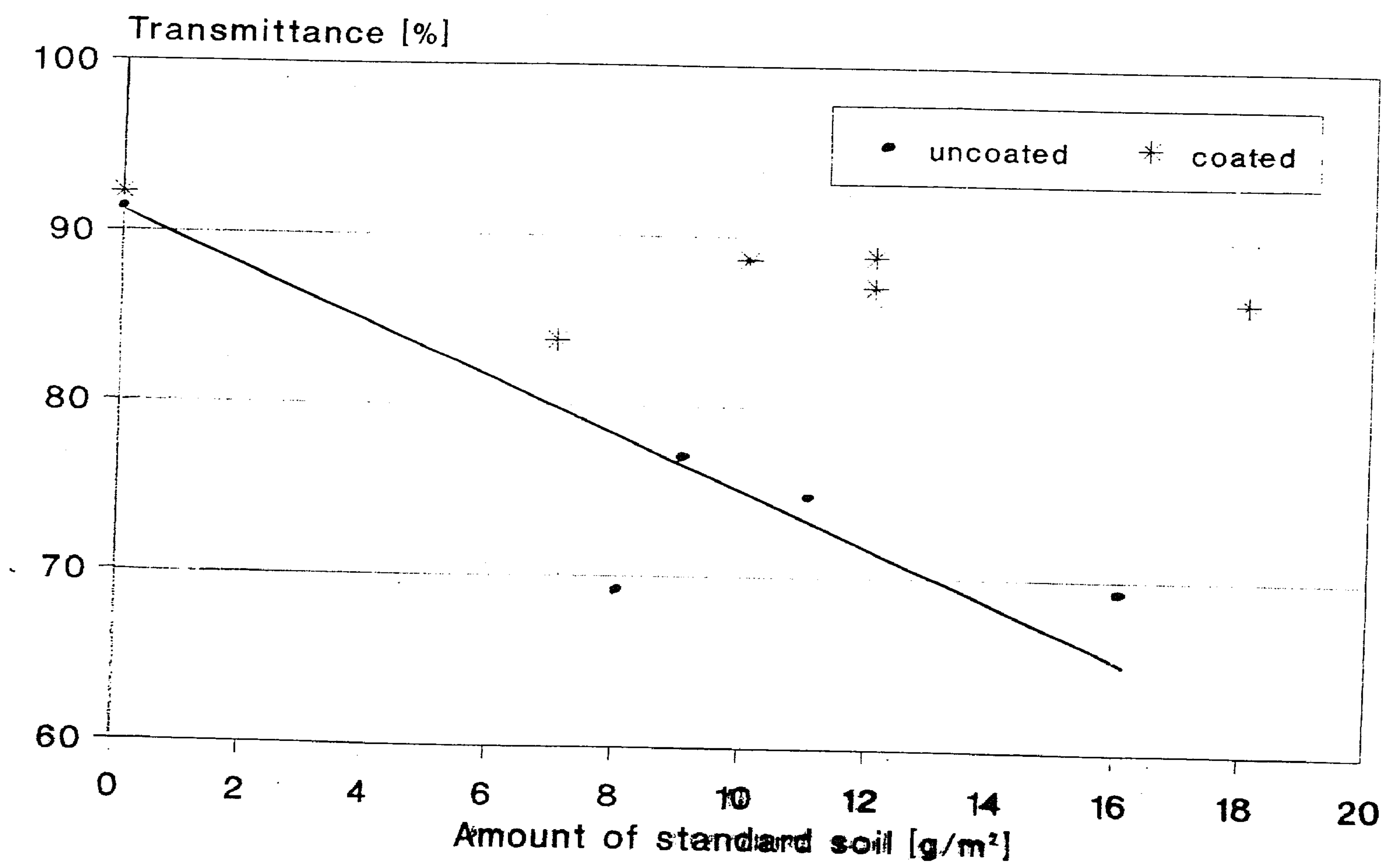
R = organische Gruppe

Organische Modifizierung

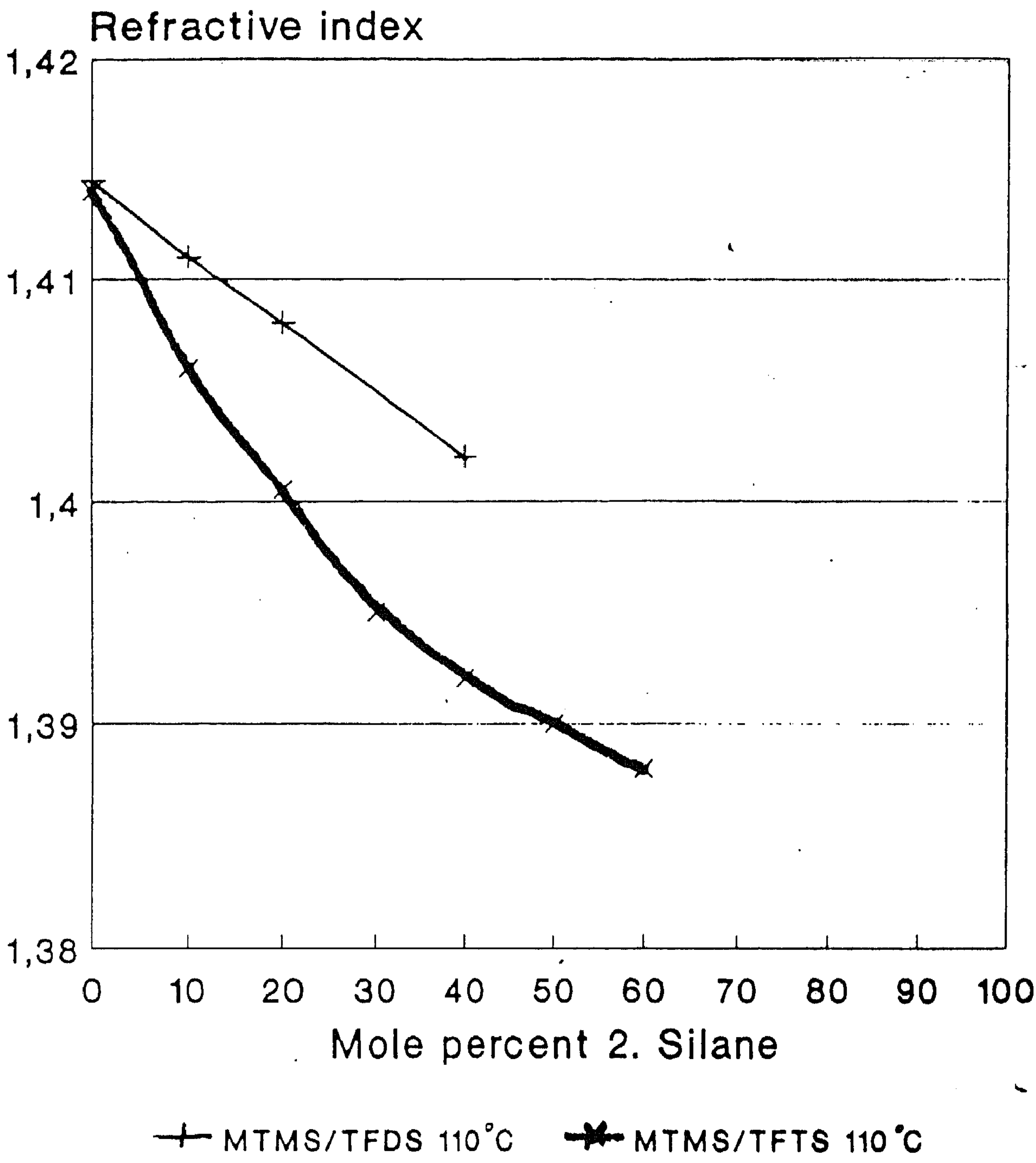
$R'\text{-}M\text{-}OR + H_2O \longrightarrow R'\text{-}M\text{-}OH$

Experimental Approach





Transmittance of uncoated and low energy coated glass samples depending on the amount of "standard soil" (an emulsion of aerosil and motor oil in water)

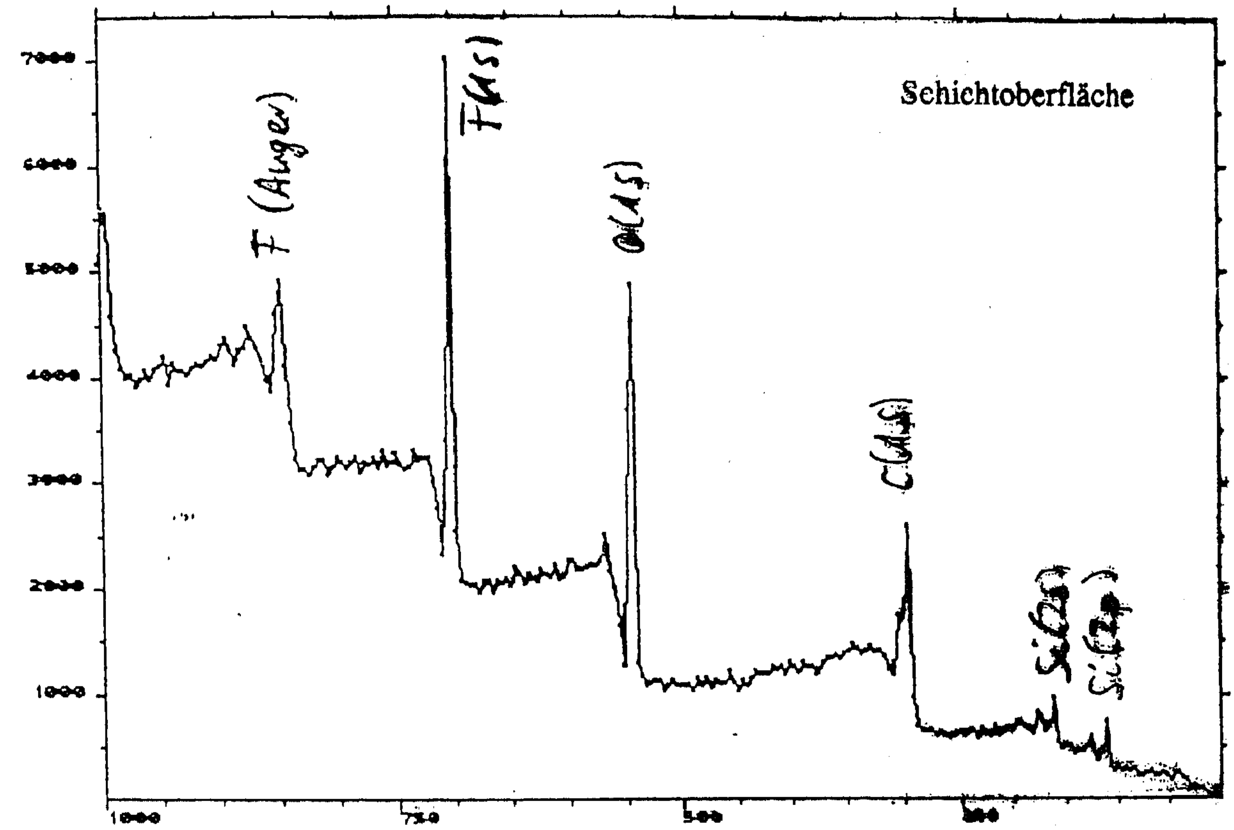


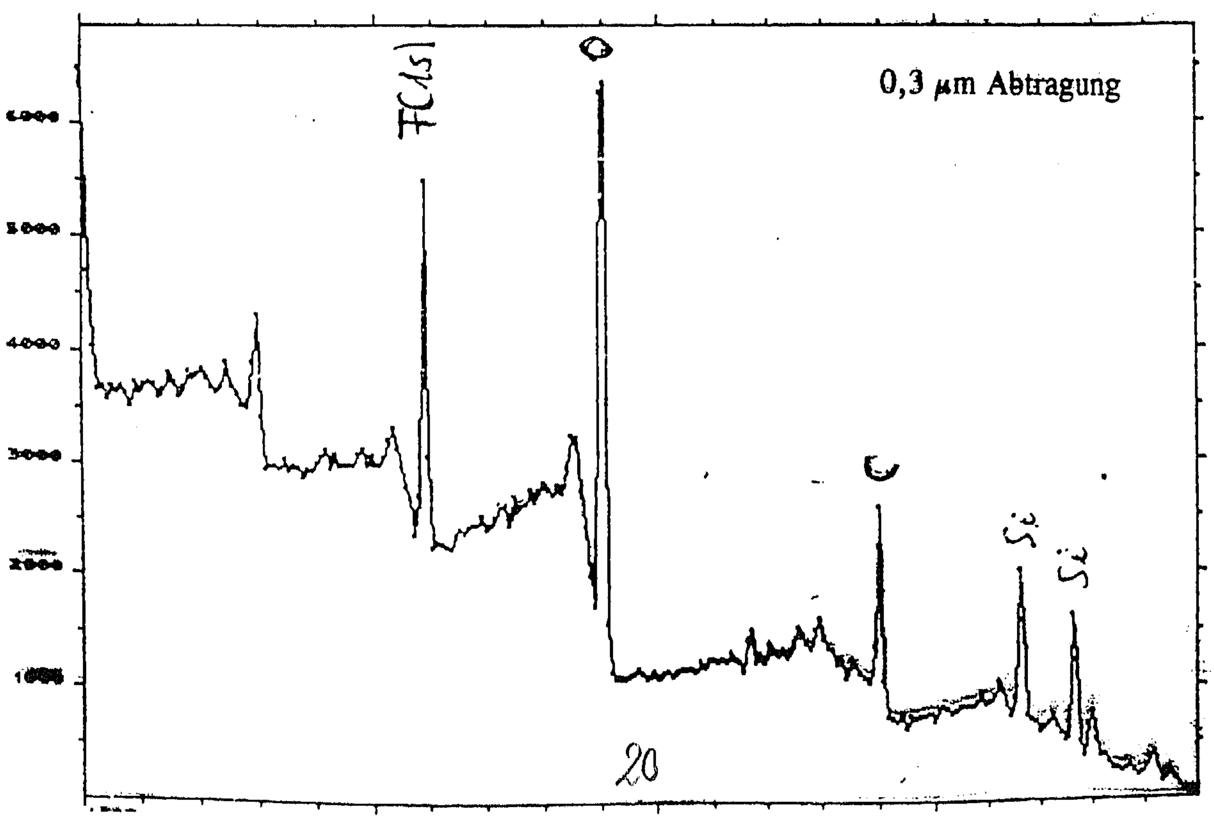
MTMS = Methyltrimethoxysilane

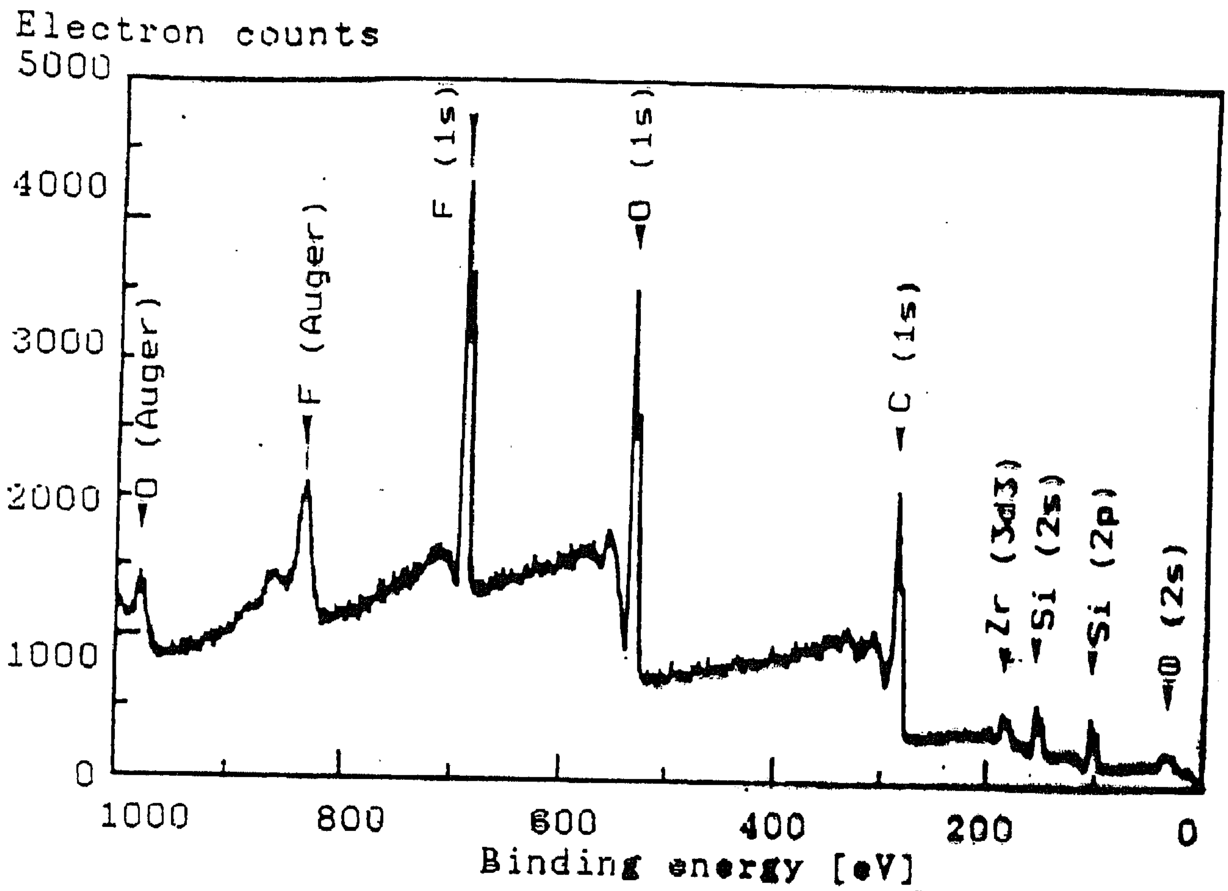
TFDS = (3,3,3-Trifluoropropyl)methyldimethoxysilane

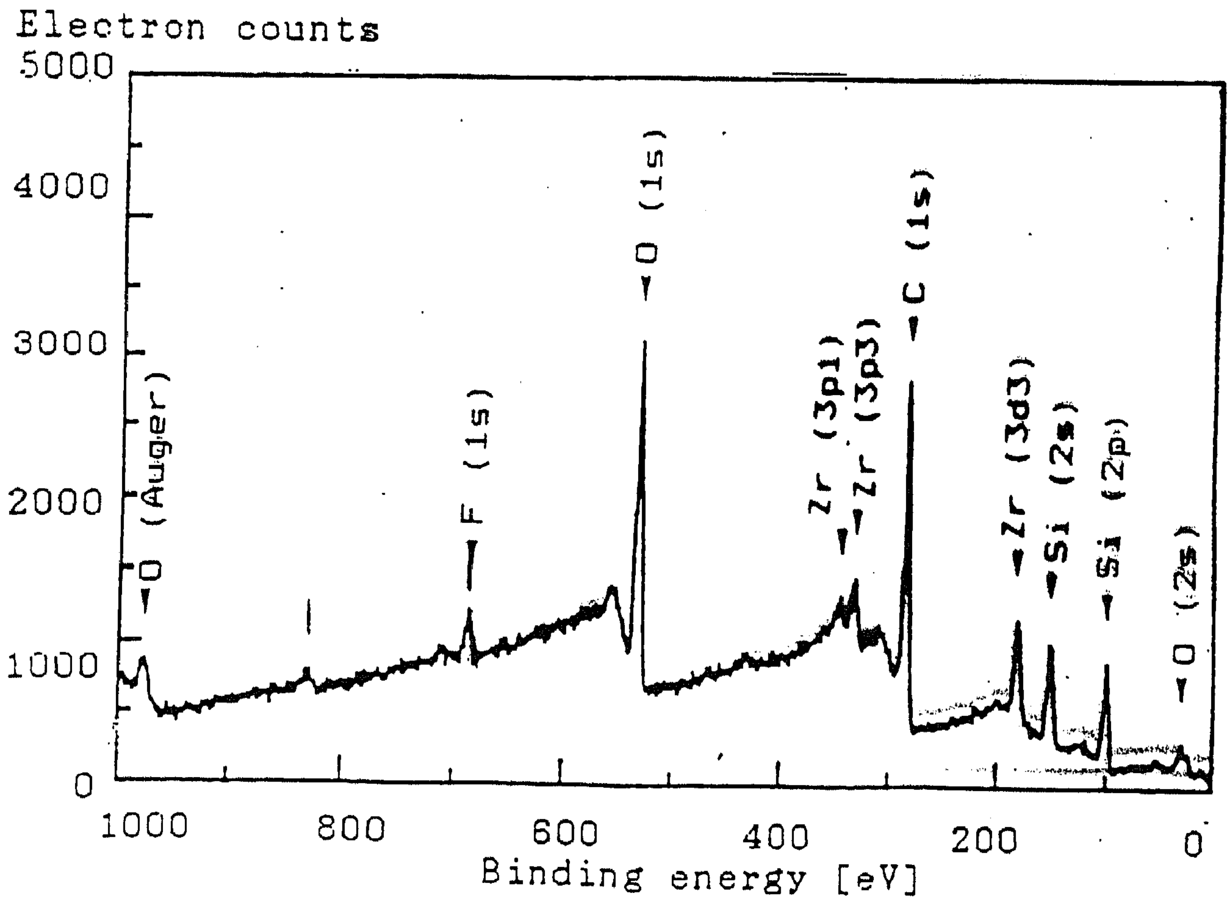
TFTS = (3,3,3-Trifluoropropyl)trimethoxysilane

ESCA - Spektren einer TFPTM - Schicht mit 40 Mol% TFPTM

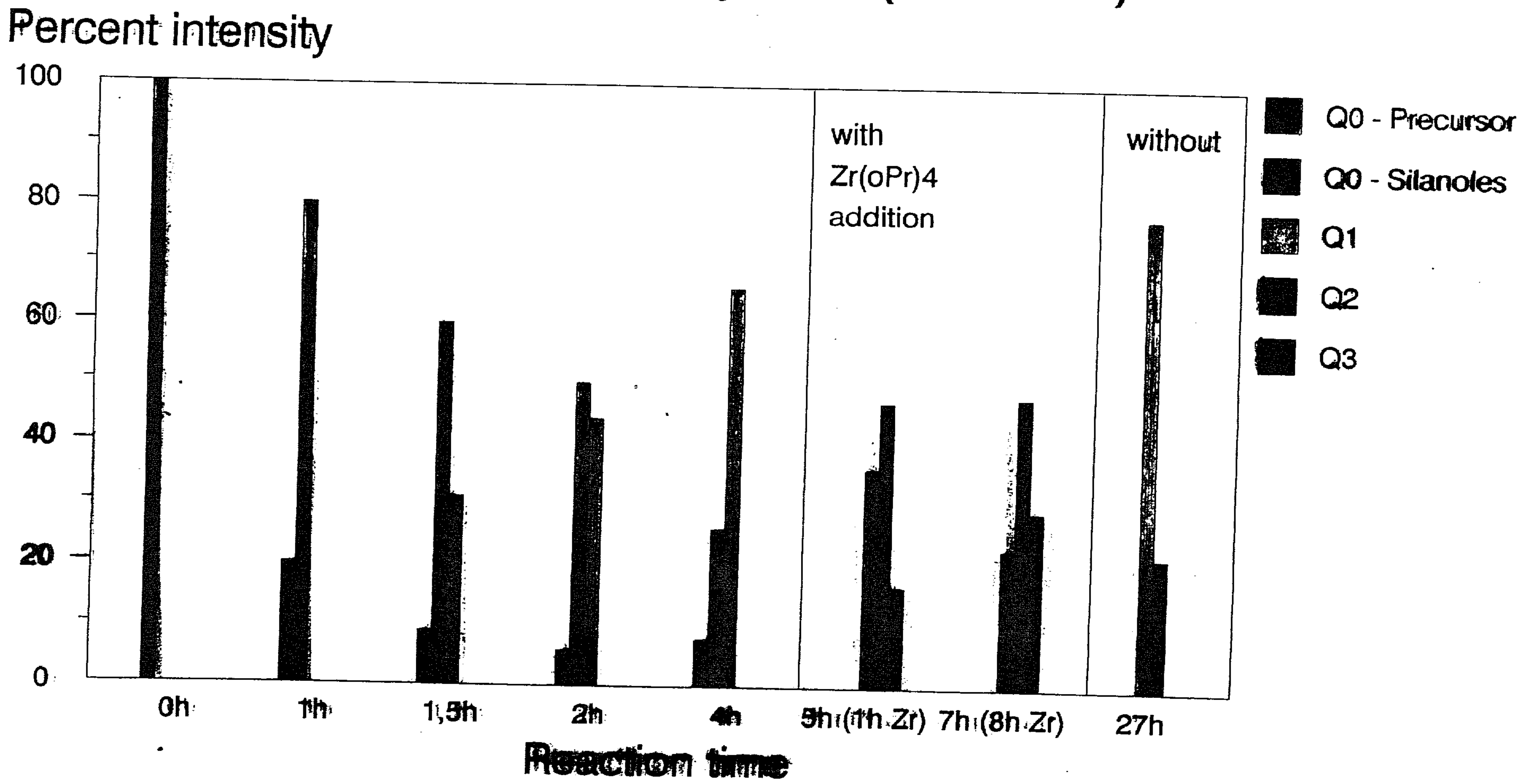




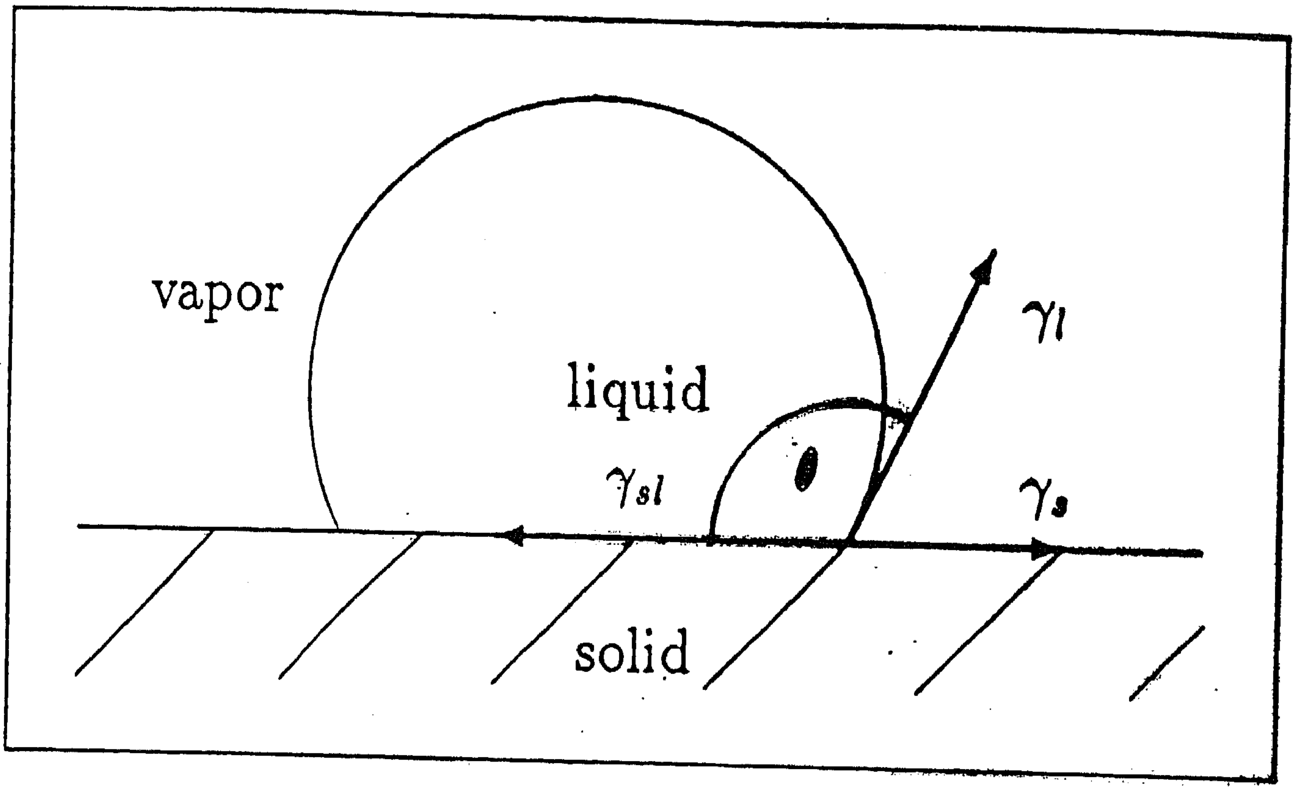

Electron counts
5000
4000
3000
2000
1000
0
F (1s)
O (1s)
O (Auger)
F (Auger)
C (1s)
Zr (3d3)
Si (2s)
Si (2p)
O (2s)
1000
800
600
400
200
0
Binding energy [eV]


Electron counts
5000
4000
3000
2000
1000
0
O (Auger)
F (1s)
O (1s)
Zr (3p1)
Zr (3p3)
C (1s)
Zr (3d3)
Si (2s)
Si (2p)
O (2s)
1000
800
600
400
200
0
Binding energy [eV]

Influence of zirconiumpropoxide addition on the hydrolysis and condensation of 3-methacryloxypropyltrimethoxysilane (29-Si NMR)



Wetting behavior



Young equation : $\gamma_s = \gamma_{sl} + \gamma_l \cdot \cos\theta$

γ_s Free surface energy of the solid

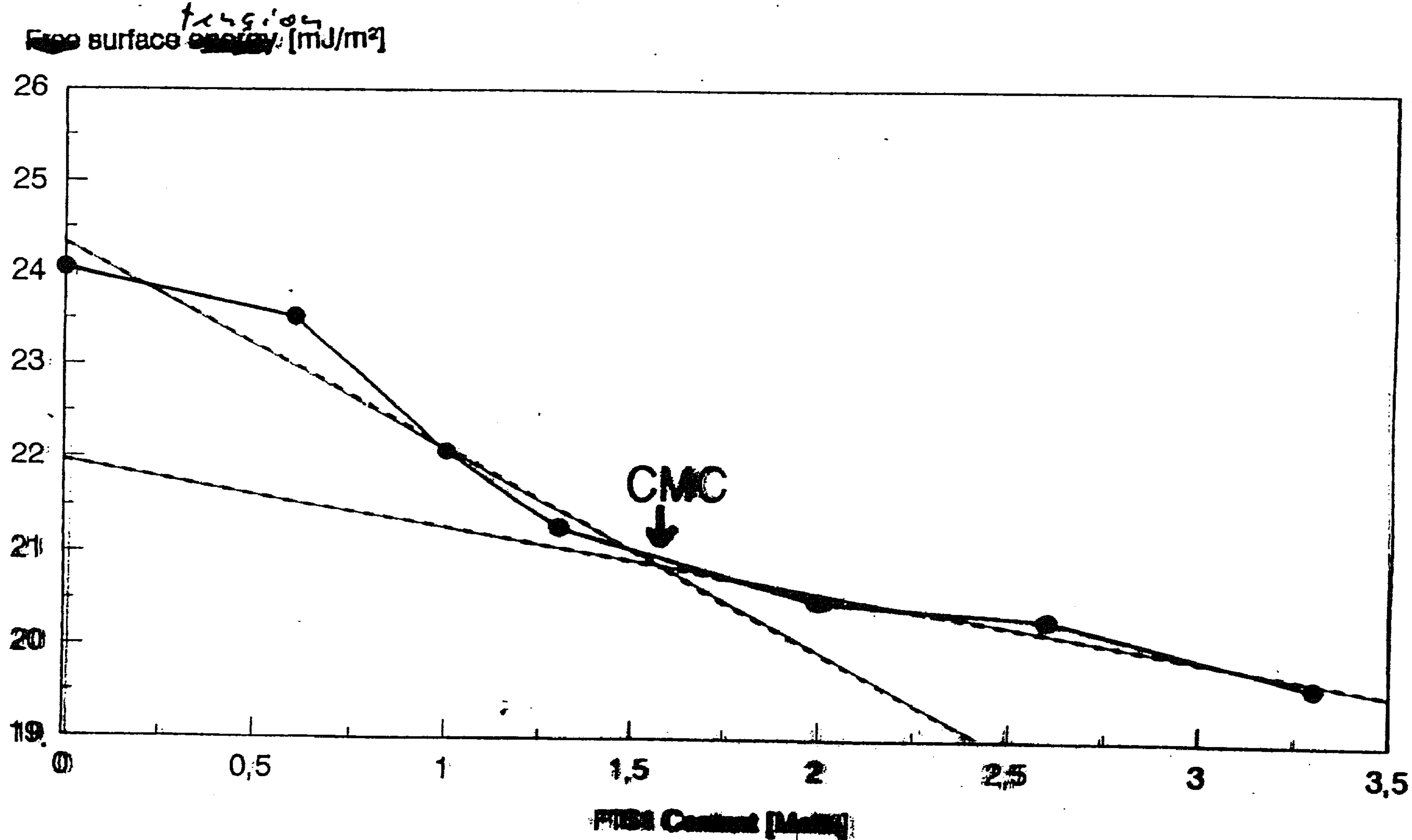
θ Contact angle

γ_{sl} Interface tension

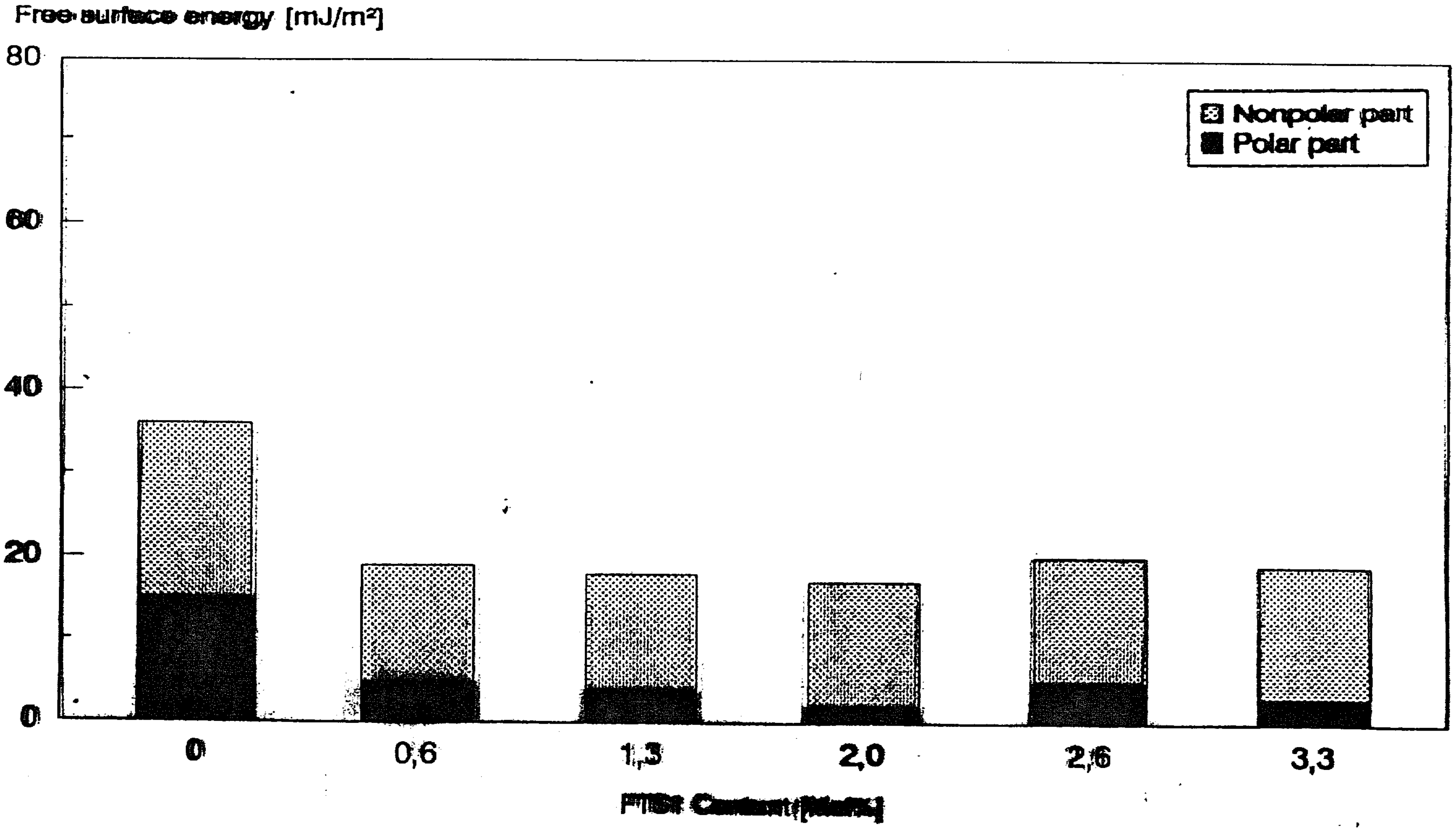
γ_l Surface tension of the liquid

$$\gamma = \gamma^P + \gamma^D$$

Surface tension of 10:2:2 molar ratio MPTS/Zr/MAS sols with increasing concentration of 1H,1H,2H,2H-perfluorooctyltri-ethoxysilane (FTS) at 20°C. Critical micelle concentration (CMC) is evaluated by interpolation

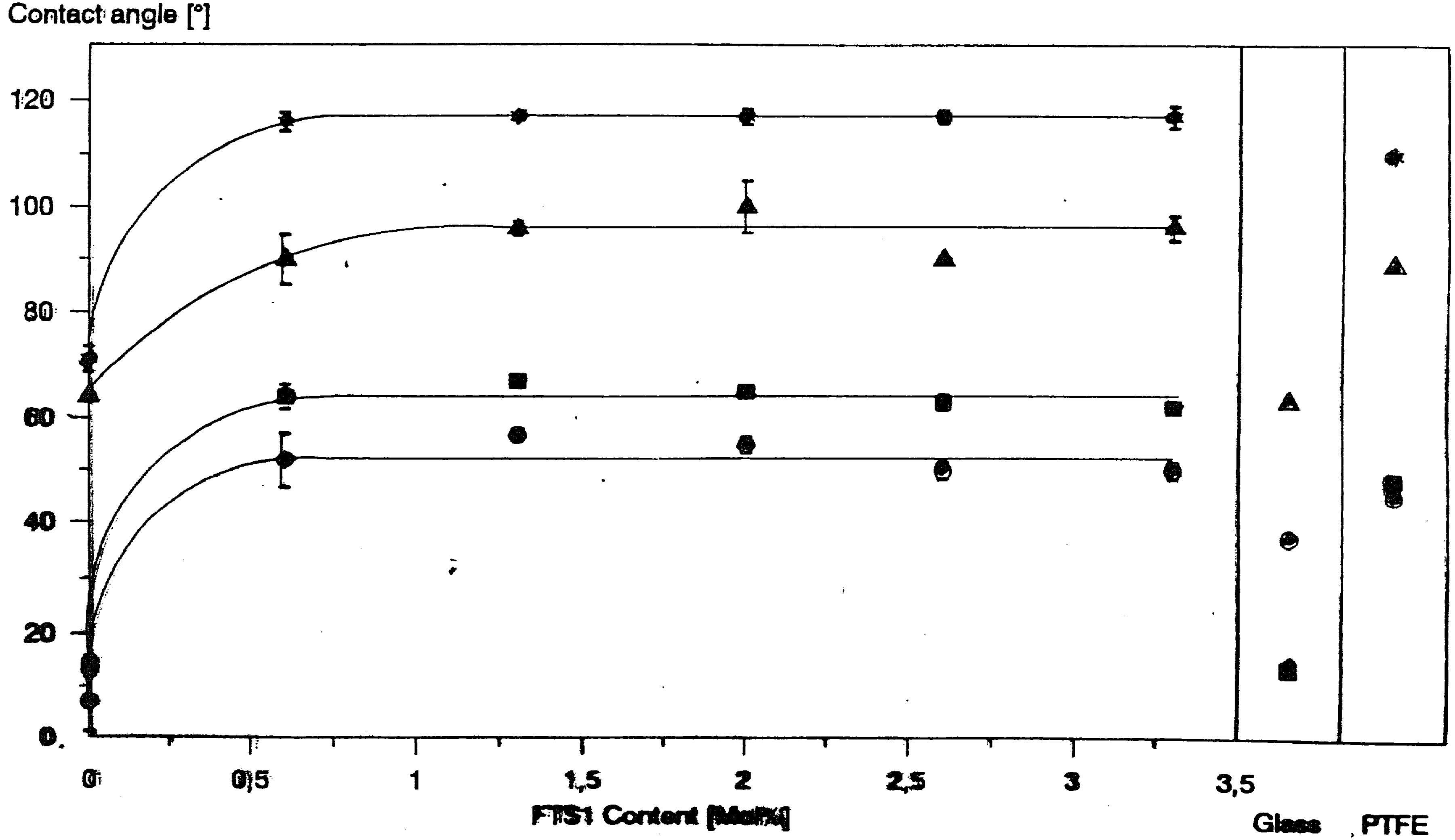


Results of free surface energy calculations from contact angle measurements for MPTS/Zr/MAS (molar ratio 10:2:2) materials with increasing content of 1H,1H,2H,2H-perfluorooctyltriethoxysilane (FTS)

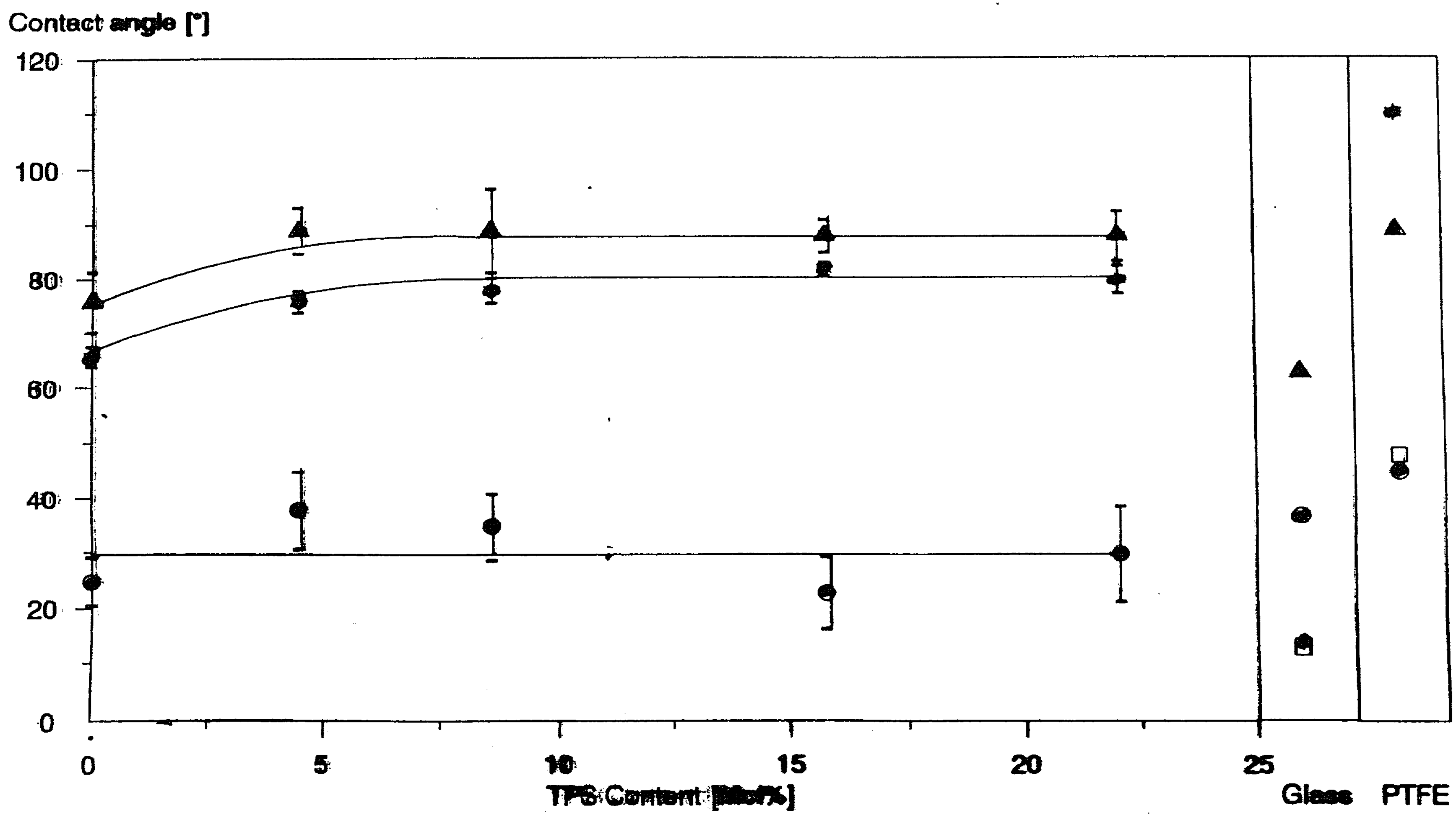


Contact angle measurements on MPTS/Zr/MAS (molar ratio 10:2:2)

Contact angle measurements on MPTS/Zr/MAS (molar ratio 10:2:2) materials with increasing content of 1H,1H,2H,2H-perfluorooctyl-triethoxysilane (FTS) for the liquids water (●), glycerol (▲), 1-octanole (●) and hexadecane (■) at 20°C



Contact angle measurements on MPTS/Zr (molar ratio 10:1) materials with increasing content of 3,3,3-trifluoropropylmethydimethoxysilane (TPS) for the liquids water (✱), glycerol (▲), 1-octanole (○) and hexadecane (□) at 20°C



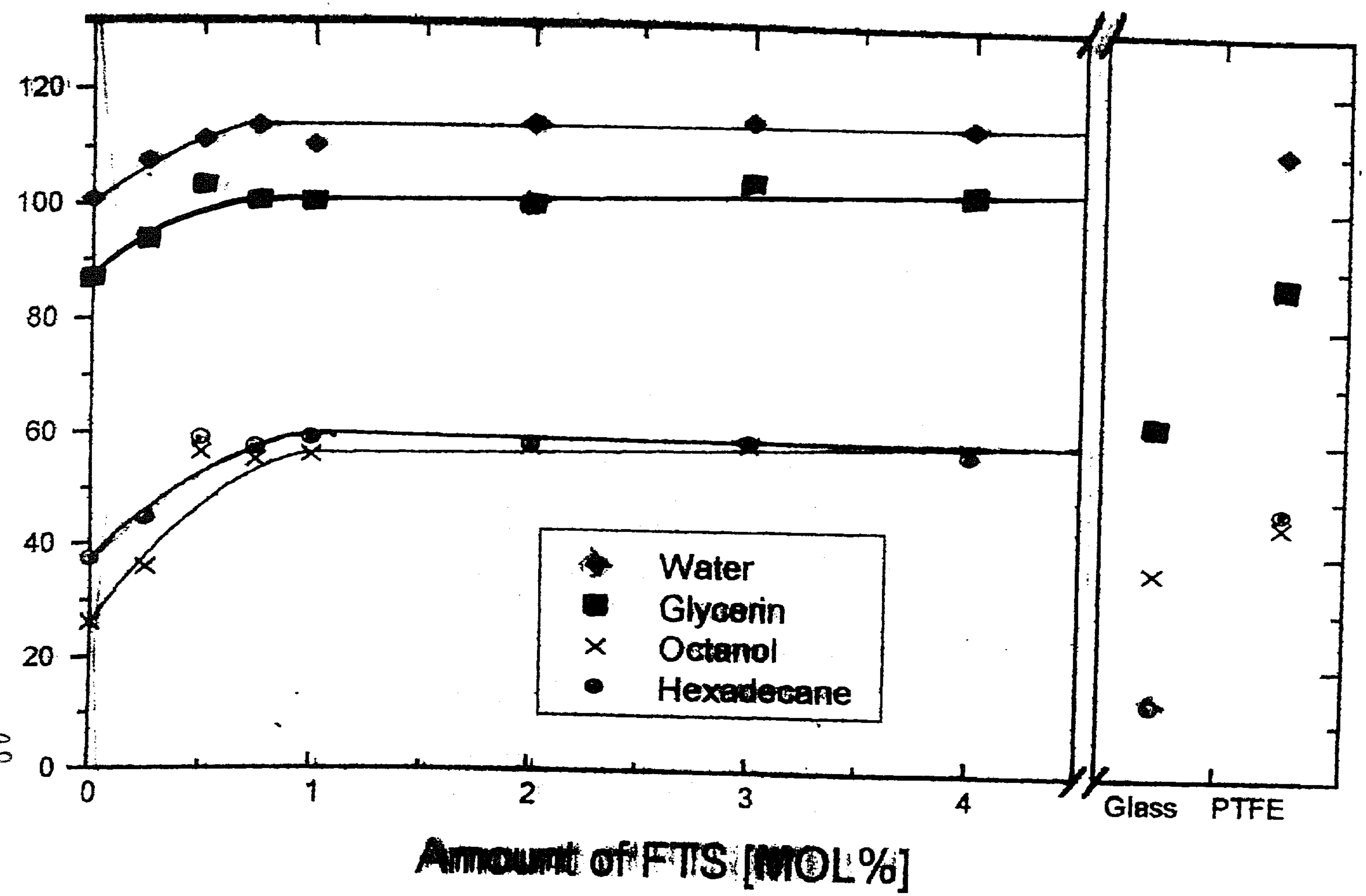
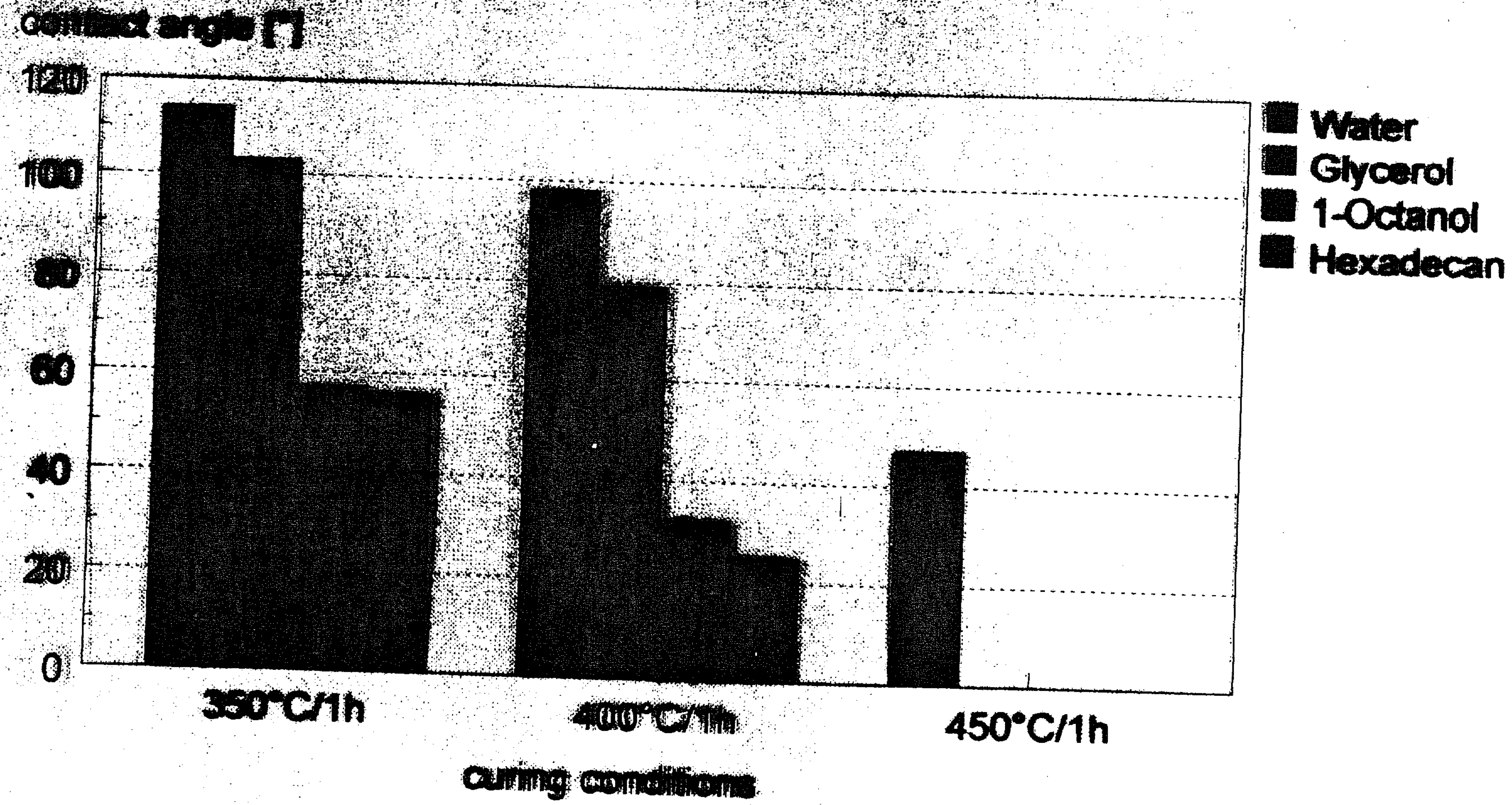


Fig. 3: Determination of the contact angles of water, glycerine, octanole, hexadecane in dependance of the molar ratio of 1H,1H,2H,2H- Perfluorotriethoxysilane (FTS) in a Methyltriethoxysilane (MTEOS)/ Tetraethoxysilane (TEOS)/ silica sol ormocer system


contact angle [°]
120
100
80
60
40
20
0
350°C/1h
400°C/1h
450°C/1h
curing conditions
Water
Glycerol
1-Octanol
Hexadecan

002.734

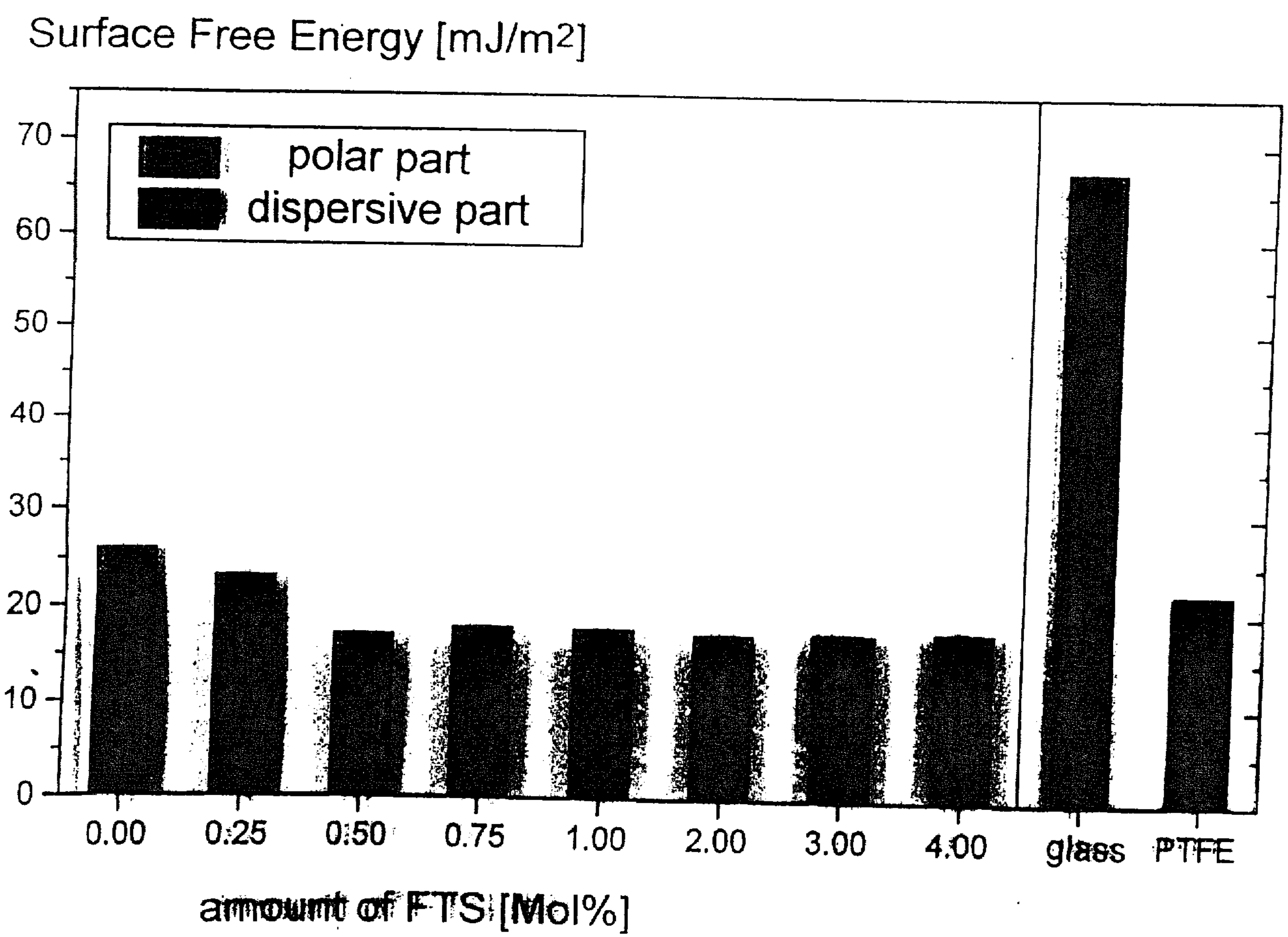


Fig. 3: Calculation of polar and dispersive part of the surface free energy of FTS containing MTEOS/TEOS coatings in comparison to glass and PTFE