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INTRODUCTION AND BACKGROUND

For many liquids an empirical correlation between *cohesive energy density* ϵ and *surface tension* γ is long since known [1]. Both quantities ϵ and γ are relative and therefore specific thermodynamic values. ϵ and γ are temperature-dependent parameters. The cohesive energy ΔE of a liquid is equal to the inner energy ΔU_V of that liquid and can be calculated from the enthalpy of vaporization ΔH_V and the work that is required to expand the vapor against the atmosphere (volume work) [2].

$$\Delta E = \Delta U_V = \Delta H_V - RT \quad (1)$$

where T is the temperature in Kelvin and R is the gas constant.

The cohesive energy ΔE related to the *molar volume* V_m of the liquid defines the quantity ϵ . Because the unit of ϵ is energy per volume the value is called *cohesive energy density*. Finally the *solubility parameter* δ (also known as HILDEBRAND-parameter) is the square root of the cohesive energy density ϵ :

$$\delta = \sqrt{\epsilon} = \left(\frac{\Delta H_V - RT}{V_m} \right)^{\frac{1}{2}} \quad (2)$$

To describe the interaction between two different solvents A and B HILDEBRAND and SCOTT introduced a new cohesive energy density ϵ_{AB} of the pairs A—B on the interface region of the solvent mixture being equal to the geometric mean of the cohesive energy densities of the pure components [2,3]:

$$\epsilon_{AB} = (\epsilon_A \cdot \epsilon_B)^{\frac{1}{2}} = \delta_A \cdot \delta_B \quad (3)$$

Equation (3) has remarkable consequences for the reliability of the whole framework of the solubility theory.

The extension of the solubility parameter δ takes account of not only the dispersion forces (δ_d), but also of the parts of the polar forces (δ_p) and the contribution of the hydrogen bonds (δ_h). It is expressed by the following summation:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4)$$

HANSEN [4] was the first who introduced this extraordinary concept to locate the solubilities of polymers in organic solvents as points in a solubility parameter plot; a cube. By tuning and successive refining the positions of each of the 32 polymers and their solubilities in 60 different solvents Hansen was able to determine for each solvent the three components δ_d , δ_p and δ_h of the HILDEBRAND-Parameter δ .

The approximation of the interaction in the interfacial region by the *method of geometric mean* is crucial and leads up to the *surface and interfacial tension* γ . Using the GIBBS-HELMHOLTZ equation of the *free energy* G ,

$$dG = dH - TdS,$$

where H is the *enthalpy*, S is the *entropy* and T the temperature, and in analogy for the interfacial region of an area A we get the thermodynamical expression for γ

$$\left(\frac{\partial G}{\partial A} \right)_{p,T,etc.} \equiv \gamma \quad (5)$$

More exactly the interfacial tension γ is named as *specific free interfacial energy*. The unit is [energy] per [surface area], i.e. abbreviated [$\text{mN}\cdot\text{m}^{-1}$].

The interfacial tension γ_{AB} in any interfacial region of two adjacent phases (e.g. liquid-liquid or solid-liquid) was first predicted for nonpolar liquids and solids by the geometric mean of the dispersion force component of the interfacial tension of both of the materials A and B:

$$\gamma_{AB} = \left(\gamma_A - \sqrt{\gamma_A^d \gamma_B^d} \right) + \left(\gamma_B - \sqrt{\gamma_A^d \gamma_B^d} \right) \quad (6)$$

where γ_A^d and γ_B^d is the part of the dispersion force of interfacial tension of the material A and B resp., with γ_A and γ_B the total interfacial tension of the pure compounds A and B. Eq. (6) was first suggested by Fowkes [5] and validated for a series of nonpolar substances.

To realize the other contributions into the eq. (6) of the interfacial tension γ_{AB} the term can be extended in the same manner as given in the following equation (7)

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\left(\sqrt{\gamma_A^d \gamma_B^d} + \sqrt{\gamma_A^p \gamma_B^p} + \sqrt{\gamma_A^h \gamma_B^h}\right) \quad (7)$$

where the super indices d , p and h indicate the parts of the dispersion and polar forces and the hydrogen bonds respectively of the interfacial tension of the material A and B resp., where γ_A and γ_B are the total interfacial tension of the pure compounds A and B.

Nevertheless of this straightforward and surely oversimplified method the calculation of the components of interfacial tension γ is possible. If material A is a solid (S), e.g. a polymer, and material B is a liquid (L) we can measure the *contact angle* Θ on the interface. The relation between $\gamma_B = \gamma_L$ of the liquid, $\gamma_A = \gamma_S$ of the polymer and $\gamma_{AB} = \gamma_{SL}$ of the interfacial region on the surface is given by the YOUNG equation

$$\gamma_S = \gamma_L + \gamma_{SL} \cdot \cos \Theta \quad (8)$$

Rename the coefficients in eq. (7), substitute eq. (7) into eq. (8) and rearrange the term yields

$$\frac{1}{2} \gamma_L (1 + \cos \Theta) = \left(\gamma_L^d\right)^{\frac{1}{2}} \sqrt{\gamma_S^d} + \left(\gamma_L^p\right)^{\frac{1}{2}} \sqrt{\gamma_S^p} + \left(\gamma_L^h\right)^{\frac{1}{2}} \sqrt{\gamma_S^h} \quad (9)$$

For a set of test liquids with known components of total surface tension γ_L , which are tabulated e.g. [6,7],

with

$$\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h \quad (10)$$

equation (9) forms a set of linear equations. The solutions are the components of the total surface tension γ_S of the polymer

$$\gamma_S = \gamma_S^d + \gamma_S^p + \gamma_S^h \quad (10a)$$

Using the results of eq. (10) and the YOUNG equation (8) we can calculate the interfacial tension γ_{SL} of the interfacial region. This procedure is also known as the *Extended Fowkes* method [8].

Solubility δ and interfacial free energy γ are two manifestations of the same intermolecular forces between different substances. Therefore the parameters δ_s^d , δ_s^p and δ_s^h should be reliably predicted by the interfacial free energy parameters γ_s^d , γ_s^p and γ_s^h respectively and vice versa. The exact relation between

$$\delta \sim \gamma \quad \text{resp.} \quad \delta^2 = (\text{const.}) \cdot \gamma \quad (11)$$

remains still unknown, but δ^2 and γ are of comparable magnitude. At the very beginning we shall set $\delta = \sqrt{\gamma}$, but are conscious of following the rather tenuous mathematical path. Nevertheless of this reduction the chemical changes up to the surface of artificially aged solids could be recognized and sufficiently explained. Consequently we transcribe the TEAS-parameter f_d, f_p and f_h [9]

$$\begin{aligned} f_d &= 100 \frac{\delta_d}{\delta_d + \delta_p + \delta_h} \\ f_p &= 100 \frac{\delta_p}{\delta_d + \delta_p + \delta_h} \\ f_h &= 100 \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \end{aligned} \quad (12)$$

into the tension-parameter t_d, t_p and t_h of the aged surface of the tested solids (polymers)

$$\begin{aligned} t_d &= 100 \frac{\sqrt{\gamma_s^d}}{\sqrt{\gamma_s^d} + \sqrt{\gamma_s^p} + \sqrt{\gamma_s^h}} \\ t_p &= 100 \frac{\sqrt{\gamma_s^p}}{\sqrt{\gamma_s^d} + \sqrt{\gamma_s^p} + \sqrt{\gamma_s^h}} \\ t_h &= 100 \frac{\sqrt{\gamma_s^h}}{\sqrt{\gamma_s^d} + \sqrt{\gamma_s^p} + \sqrt{\gamma_s^h}} \end{aligned} \quad (13)$$

Experimental

A maple veneered 3 mm – plywood carries a multi-layered finish, which is applied with a red sable hair brush. The layers are sanded in between. Six different varnishes are used:

- cold pressed linseed oil, natural
- cold pressed linseed oil with a siccative (Manganese(II)acetylacetonate)
- Cellulose nitrate (pure), dissolved in Acetone/Ethyl acetate, diluted with Ethanol to a 10% solution, butanol was added to improve the film formation
- Dammar
- bleached shellac, wax free
- so called Button lac (raw shellac, washed)

All of the natural resins are dissolved in Ethanol (10% solutions). The storage of the samples (size: 100 x 40 mm) takes place in an exsiccator at room temperature and about 55 % relative humidity (above a saturated Magnesium nitrate hexahydrate solution) in darkness.

One batch of samples are treated at a time by a mercury low pressure radiator (“Puritec” NSE 11-270 G 23, Radium, Germany) with 90 %-emission at 254 nm and increased temperature (50 °C ± 4 °C). Humidity is not controlled. The storage time of the samples is for the first batch treated 11 and for the second one 12 weeks. The samples are irradiated at higher temperature for 16 hours (± 1 h) and stay for 8 hours (± 1 h) under room conditions. In this time contact angles are measured.

Contact angle measurement occurs by the Sessile Drop Method with a video-based optical contact angle meter, equipped with an electronic syringe unit (OCA 15plus, DataPhysics Instruments GmbH, Germany). The measurement is carried out at room conditions. SCA 20 software, Version 1.6, is used to operate the instrument and to calculate contact angles as well as free surface energy of the solid samples.

Settings :

- Syringe type: Hamilton 1750 TLL (500 µl) used with a replaceable dosing needle with a inner diameter of 0.1 mm (Art.-No. 5132-1/4-B, GLT mbH, Germany)
- Drop type: normal drop
- Drop volume: 5 µl
- Dosing rate: 4 µl/s
- Frame grabbing time 10 s, 25 images/s (except measurements with *n*-decane: frame grabbing time 3 s, 50 images/s)
- Calculation method for the sessile drop: circle fitting (neglects gravity)
- Liquids: water, ethylene glycol and *n*-decane

Each sample is measured 10 times at different spots, further calculations are based on the average of the results above.

RESULTS AND DISCUSSION

The summarized values in table 1 together with the contact angles Θ in table 2 enable to calculate the contributions of dispersion forces γ_s^d , polar forces γ_s^p and hydrogen bonding γ_s^h to the total interfacial free energy.

TAB. 1: Set of test liquids (L) and their total surface tension γ_L and contributions γ_L^d , γ_L^p and γ_L^h , in units of [mN/m] (see eq.(10))

Ref.	test liquid (L)	γ_L	γ_L^d	γ_L^p	γ_L^h
[8]	Water (A)	72,80 ± 0,05	29,10	1,30	42,40
[8]	ethylene glycol (B)	47,70	30,90	0	17,60
[6]	<i>n</i> -decane (C)	23,83 ± 0,10	23,83	0	0

TAB. 2: Average value of contact angles θ of the three test liquids on different surface materials and results of the calculation by the method of Extended Fowkes (see. eq. (9))

	ageing [h]	θ_A	θ_B	θ_C	γ_s^d	γ_s^p	γ_s^h
Cellulose nitrate	0	76,9 ± 0,4	49,4 ± 0,8	8,2 ± 1,2	23,51	2,18	9,65
	16	47,7 ± 3,4	31,9 ± 3,8	7,7 ± 0,6	23,62	25,47	19,15
	33	24,9 ± 0,8	17,8 ± 0,7	6,3 ± 0,5	23,65	72,07	21,62
	49	23,9 ± 0,7	19,1 ± 1,0	7,6 ± 0,2	23,61	117,58	22,53
Shellac	0	66,3 ± 0,7	36,3 ± 1,0	8,3 ± 0,4	23,54	0,24	13,66
	16	65,6 ± 0,1	37,6 ± 0,4	8,6 ± 0,3	23,57	5,17	15,11
	33	65,7 ± 1,8	37,8 ± 1,0	7,9 ± 0,7	23,58	4,32	15,17
	49	54,0 ± 1,1	33,2 ± 1,6	11,9 ± 1,3	23,48	11,66	18,02
Dammar	0	69,2 ± 0,5	56,8 ± 0,5	8,4 ± 0,4	23,59	40,95	23,39
	16	52,9 ± 0,7	20,1 ± 0,7	7,0 ± 0,4	23,63	1,2	22,05
	33	24,9 ± 0,7	23,3 ± 0,5	7,8 ± 0,9	23,61	108,19	21,49
	49	37,8 ± 7,6	29,1 ± 1,6	9,4 ± 0,4	23,54	94,54	20,47
Linseed Oil, cold pressed	0	92,3 ± 1,9	77,4 ± 1,3	7,7 ± 0,1	22,76	55,14	0,07
	16	81,9 ± 0,9	58,5 ± 0,5	5,7 ± 0,4	23,39	53,63	1,34
	33	78,2 ± 1,5	55,1 ± 0,3	6,6 ± 0,5	23,43	34,65	3,72
	49	75,2 ± 1,6	55,1 ± 1,1	6,1 ± 0,1	23,48	61,17	3,37

The conditions of artificial ageing are very tough and intensive (moisture 50% r.h., temperature 50°C and short wave light 254 nm). The degradation on the surface of the chosen materials cellulose nitrate, shellac, dammar and linseed oil is obviously seen in the increase of the γ_s^p values. In contrast to the strong time-dependence the changes of the polar forces represented by γ_s^p the contribution of dispersion is remarkable constant and of unexpected magnitude. The dispersion forces of all of the investigated materials are in the range of about 20 mN m⁻¹. Obviously the ubiquity of the dispersion forces in any kind of matter are responsible for such consistent behavior. Dispersion forces exist in all types of matter and always give an attractive force between adjacent atoms or molecules no matter how dissimilar their chemical natures may be.

So it might be possible to approximate the unknown volume element or *molar volume of solids* especially of the polymers. For instance the CH₂ group in saturated hydrocarbons or the CH group in aromatics have nearly the same radius as the water molecule [5].

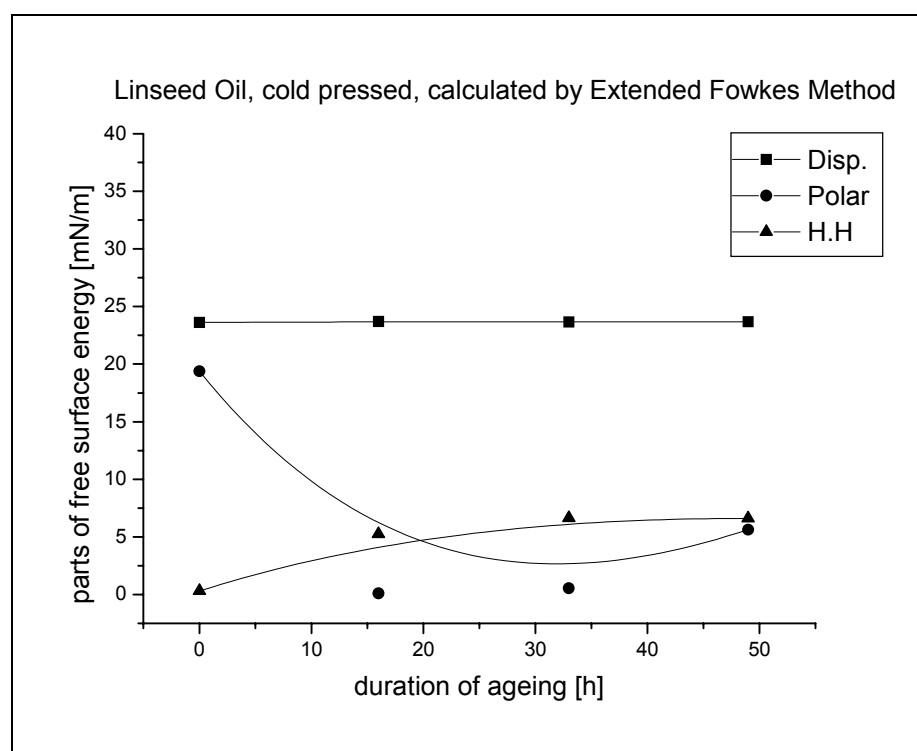


FIG. 1 Contribution of γ_s^d (■), γ_s^p (●) and γ_s^h (▲) to the total free surface energy γ_s of a film of linseed oil (air, light 254nm, 50% r.h. 50°C)

The changes in γ_s^p and γ_s^h are better illustrated by graphs. Fig. 1 shows an interesting behavior of decreasing in the polar component and a slightly increase in the hydrogen bonding part of the free surface energy of the linseed oil film. Normally the polar forces and the free surface energy γ_s^p increase during the ageing process. On the other hand the film seems to be stable to polar and unpoloar

solvents. In comparison with natural aged linseed oil we calculated according eq. (13) the t -parameter and entered the values into Fig. 2 which was taken from the literature [10]. The only thing that fits is the appropriate location in the chart far away from the shown swelling regions of the natural aged film.

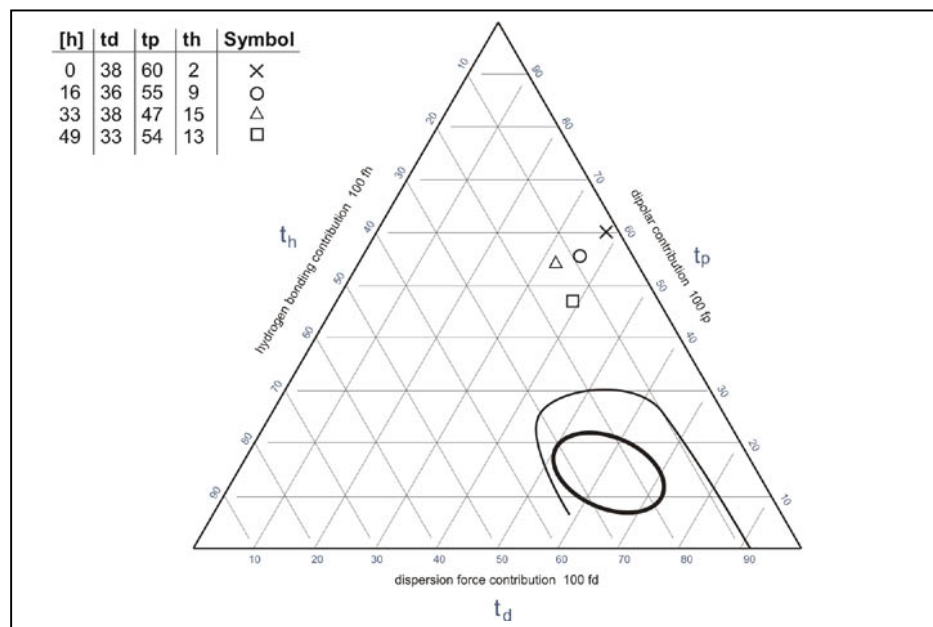


FIG. 2 Swelling behavior of polymerised linseed oil films Contours at 60% swelling are shown for a film aged 27 weeks (—) and a film aged 14 years (---), data from Stolow [10]; the t -parameter (see eq. (13)) of the own linseed oil film are entered: (○) untreated, (⊠) after 16 hours, (⊞) after 33 hours and (⊐) after 49 hours of ageing

An example for a strong artificial aged material is cellulose nitrate which is illustrated in Fig. 3 and 4. The constant values of γ_s^d and the moderate growth in γ_s^h ist dominated of an extraordinary increase of the γ_s^p at last over 100 mN m^{-1} .

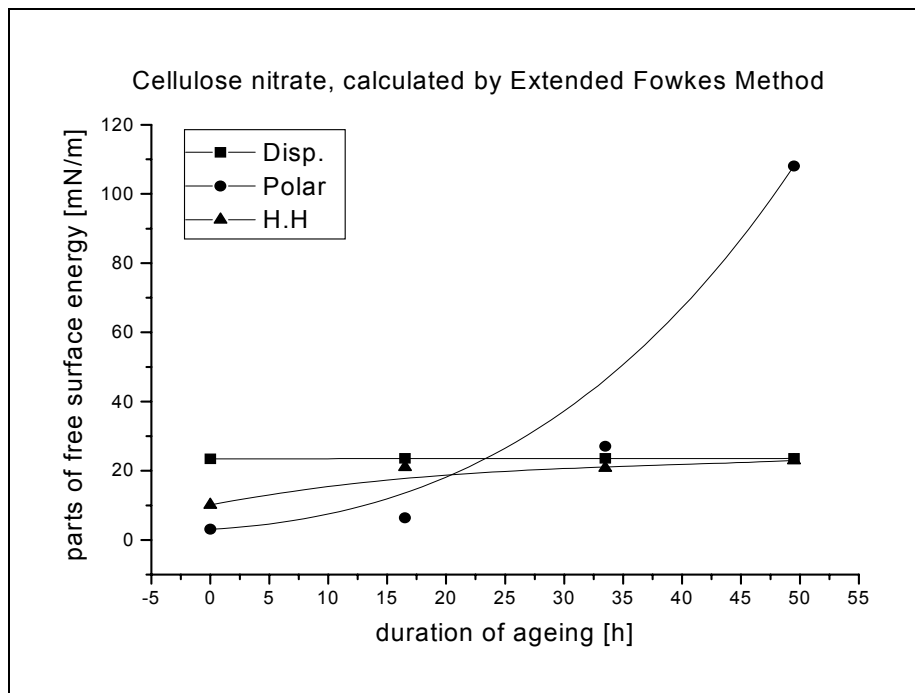


Fig. 3 Contribution of γ_s^d (■), γ_s^p (●) and γ_s^h (▲) to the total free surface energy γ_s of a film of cellulose nitrate (air, light 254nm, 50% r.h. 50°C)

The well-known instability and photooxidative degradation of cellulose nitrate is yet visible during the last measurements (over 30 hours of ageing). The test liquids water and ethylene glycol dissolve the stressed cellulose nitrate rapidly. The calculated t -parameters (eq. (13)) are added into the solubility chart of a commercial cellulose nitrate (see Fig. 4).

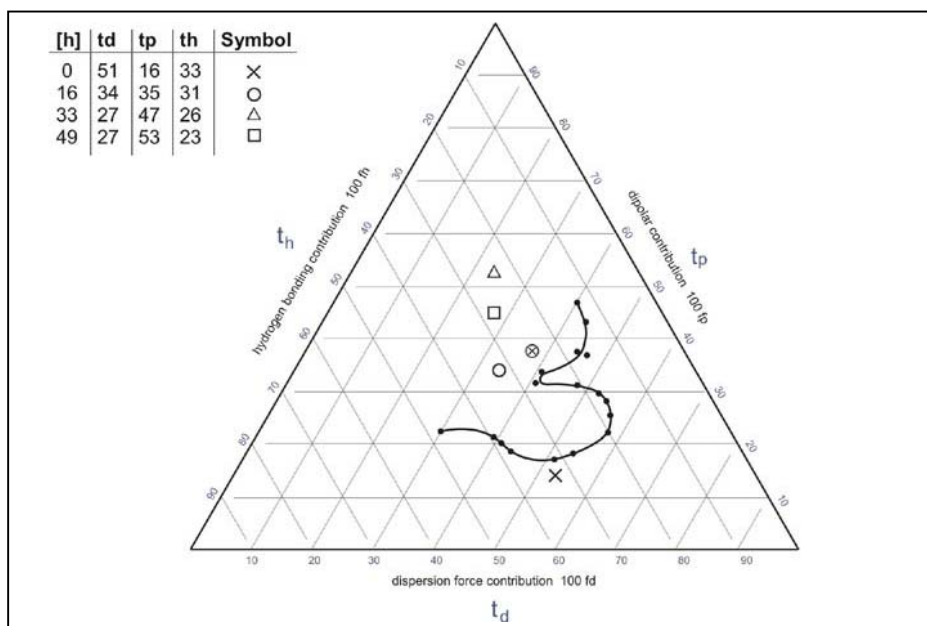


FIG. 4 Solubility of cellulose nitrate (CN), data (★) from Hansen [10]; the t -parameter (see eq. (13)) of the own CN film are entered: (○) untreated, (◻) after 16 hours, (△) after 33 hours and (p) after 49 hours of ageing. The point (⊗) marks another solubility of CN (Ref [11]): $\delta_{CN}^d=15.4$, $\delta_{CN}^p=14.7$ and $\delta_{CN}^h=8.8$, and according eq. (12) $f_d=39.6$, $f_p=37.8$ and $f_h=22.6$

Only the untreated cellulose nitrate is behind the frontier of solubility. The following values of the t -parameter clearly move in the direction of the strong polar region of the solubility chart. Fig. 3 and 4 correspond with each other.

As in Fig. 5 seen the dammar shows a more complex behavior of the changes in the parts of the attractive forces relating to the total interfacial tension γ_s . The contributions of the dispersion forces and the hydrogen bonding are the way as just developed in the examples of the linseed oil and the cellulose nitrate. Nearly constant in the amount of γ_s^d and only a slightly increase in the γ_s^h values during the ageing. Also the magnitude of these values are comparable with the two former discussed materials. In the case of the polar forces we are concerned about the reliability of the measured contact angles and the calculations. It is unlikely that the time depending function $\gamma_s^p = \gamma_s^p(t)$ goes through a minimum, but rather the course is S-shaped and reaches a plateau. The assumption of such a S-shaped run of $\gamma_s^p(t)$ could be strengthened by calculations which make use of the harmonic mean method [7].

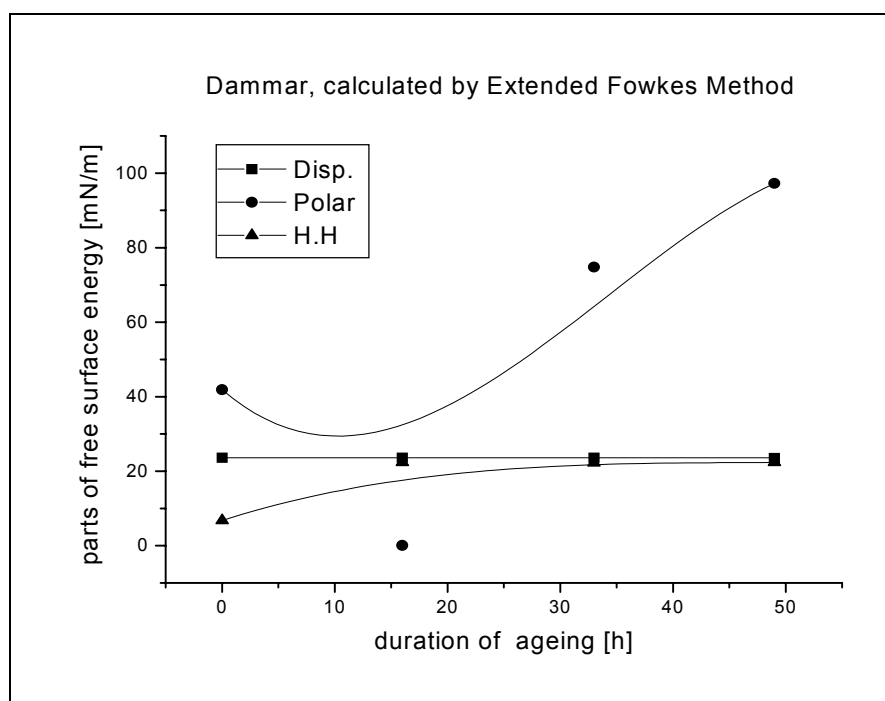


FIG. 5 Contribution of γ_s^d (■), γ_s^p (★) and γ_s^h (π) to the total free surface energy γ_s of a film of dammar (air, light 254nm, 50% r.h. 50°C)

Also the t -parameter are strong influenced by $\gamma_s^p(t)$ as seen in Fig. 6. In that respect it is interesting that the narrow margin of solubility and the predicted limit of natural ageing of dammar varnish [10] seem to be too restrictive. The subject is important and further discussion and experimental proof are necessary.

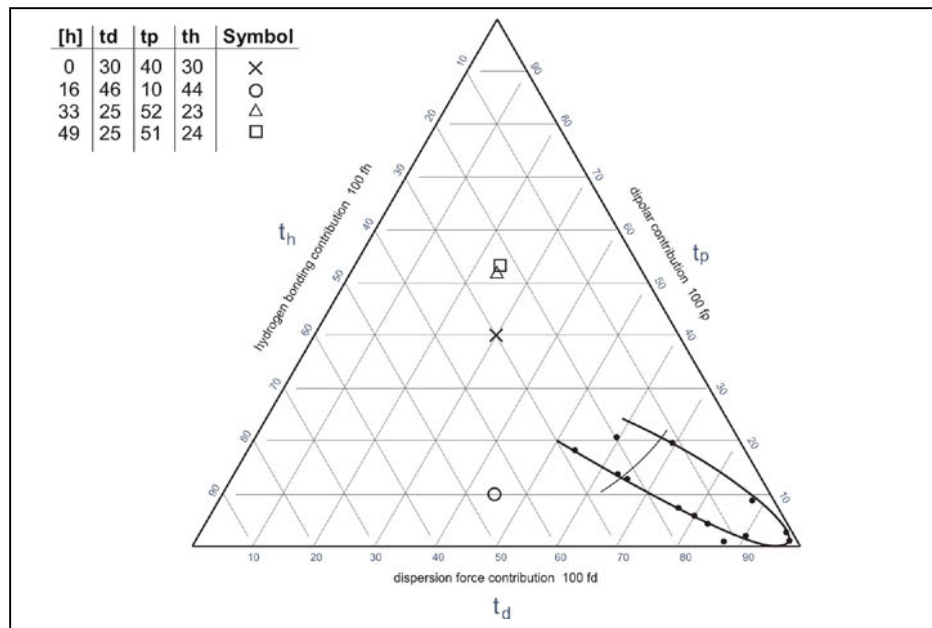


FIG. 6 Solubility of dammar resin, data (★)from Mantell [10]; the crossing (—) indicates the approximate limit of solubility when exposed to light and oxidation equivalent to 100 years on a gallery wall (Feller and Curran, 1975, [10]) the t -parameter (see eq. (13)) of the own dammar film are entered: (○) untreated, (○) after 16 hours, (△) after 33 hours and (□) after 49 hours of ageing.

CONCLUSIONS

The results of this first study shows the following.

- 1.) The estimation of the solubility parameter δ of polymers using the measured interfacial tension γ is in principle possible.
- 2.) The contribution of the polar forces of attraction in the interfacial region has the strongest influence on the t -parameter.
- 3.) The time dependence of the function $\gamma_s^p = \gamma_s^p(t)$ is an important characteristic to validate the changes of the chemical and physical conditions on the artificial aged polymer surface.
- 4.) There is a possibility that the calculation by the method of extended Fowkes could be refined using more liquids with different and non zero contributions in all parts of the interfacial free energy γ_L .
- 5.) Progress and continue work are necessary and should combine the harmonic and geometric mean method to receive a reliable set of γ_s^d , γ_s^p and γ_s^h values of the aged polymer surface.

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