研究論文

A Model for the Initiation of Explosives
—high and low velocity detonation—

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Of some recent papers[1] of the author a summary is presented about initiation-phenomenas and the stability of detonations. BOWDENs hot-spots are substantiated as hot-spots of high acoustic power which may get particle-velocities different from the surrounding medium and may overcome the shock velocity causing an infinite duration of the particles in the shock-zone. According to this and rheological criterias high- and low-velocity detonation may be understood.

It is wellknown there is no model for explaining initiation-phenomenas. According to the classical hydrodynamic theory shock-propagation is considered to be the fastest event and should influence the original explosive.
The propagation of detonation is characterized by the CHAPMAN-JOUGUET-state, but this state is not wellknown because it is described between the reacted and original explosive.
As it is assumed, mainly from BOWDEN, that cavities act as centes of initiation, also experimentally realized, the supposed adiabatic temperature-rise is too low to explain the high reaction-rates. Therefore the adiabatic model had been favoured more by others than by Bowden himself. Recently an extended critizism-mainly from russian authors-rose concerning the adiabatic mechanism. To put these difficulties aside we should mainly consider the shock-front and the region of shock-rise, and if doing so, we get the problem of initiation-mechanism.

In this theory summarized here, the BOWDEN-difficulties don't exist, the shock-propagation must not be the fastest event, the formerly important role of hot-spot-temperature is substantiated as a hot-spot of high acoustic power to be dissipated in the immediately surrounding medium and a lot of still not understandable phenomenas may be explained and moreover by consideration of the rheological properties of the explosives a criterium of the stability of the high-(HVD) and low-velocity-detonation (LVD) is obtained.

Assuming an infinite medium with a discontinuity in it exposed to an acoustic field, two extreme cases are possible :

a) Discontinuity very small in respect to the wave-length,

b) Discontinuity similar to or greater than the wave-length.

Case a) had been treated by Skudrzyk[1], which found, that the discontinuity may reach a particle-velocity different from the surrounding medium in some circumstances, depending on the size of the (spheric) discontinuity with diameter 2R, the viscosity and density of the surrounding medium y/ρ_∞,

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the density of discontinuity ρ^1, and the stimulating frequency f_1 of the acoustic field. Whether the discontinuity is fixed by viscous forces or gets a mobility in respect to the surrounding medium is defiined by ROTH's number

$$\Omega = \frac{f_1}{f_0} \qquad (1)$$

where f_0 is a characteristic frequency determined by

$$f_0 = \frac{3y/\rho_\infty}{2\pi R^2} \qquad (2)$$

for the case where discontinuity is a first order acoustic oscillator (pulsating 8). Principally ROTH's number has the similar meaning like REYNOLDS' number and determines the fraction of the energy of acceleration to viscous dissipation of the discontinuity in the matrix.

It is obvious that no discontinuity-moving occurs if viscous forces are dominant and the material shows in this case a homogeneous dynamic behaviour. If, however, viscous forces are overcome by forces due to inertia of the discontinuity, its particle-velocity of zero-density, as example, doesn't reach an infinite value-according to momentum-because of its acoustic mass due to its acoustic oscillations.

Fig. 1 shows the mobility-ratio in general as a function of ρ^1/ρ_∞ and Ω. A discontinuity of zero-density (bubble) ultimately reaches 3-times the particle-velocity of the surrounding medium if forces due to inertia ($\Omega > 10^3$) are dominant.

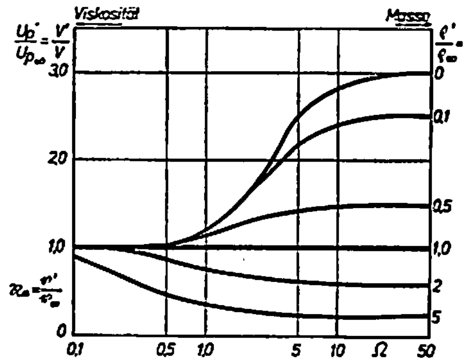

Fig. 1 Skudrzyk-solution of the mobility ratio of discontinuity and matrix

Moreover the SKUDRZYK-solution also shows an imaginary part of the particle-velocity-ratio. This part represents the interaction of the oscillating spheres with the surrounding medium, see fig. 2, a COLE-cirele is built up by the real and imaginary part of the complex particle-velocity-ratio.

Assuming an isomorphism between shock-

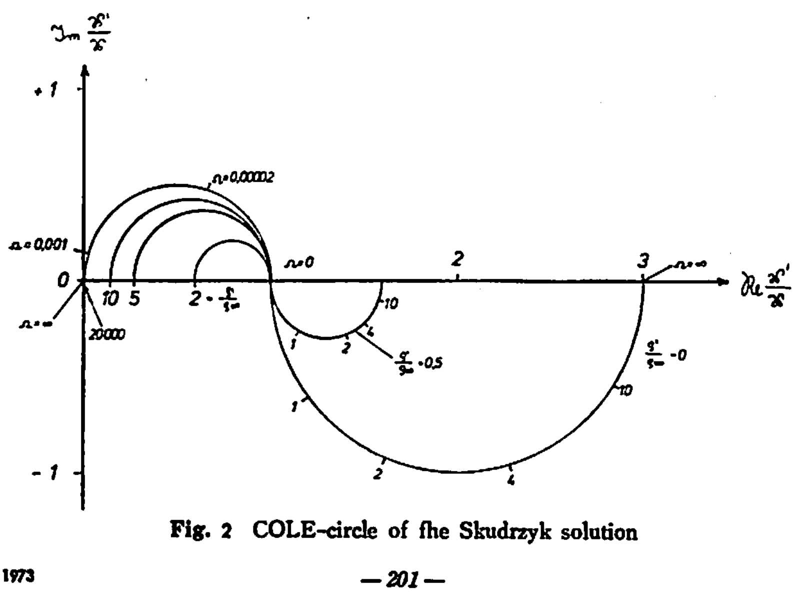

Fig. 2 COLE-circle of fhe Skudrzyk solution

and acoustic-pressure

$$p - p_0 = \rho_\infty u_s u_p \text{ (shock)} \qquad (3)$$
$$p - p_0 = \rho_\infty c v \quad \text{(acoustic)}$$

it is to see, that shock-particle-velocity and acoustic-particle-velocity correspond to

$$u_p \hat{=} v \qquad (4)$$

where c is the constant, or nearly so, sound-velocity and u_s the pressure-dependent shock-velocity.

Now we have to treat this case for applicability to the case of a shock. A nonreactive shock in an acoustically real material can't be considered as indefinitely steep, since every material shows an increasing acoustic attenuation with increasing frequency due to viscosity. Assuming a step-function should be transmitted through a real material, we assume for cases of simplicity, that no loss should occur below the limiting frequency f_1 but complete absorption above f_1, KÜPFMÜLLER's step-response-function shows the solution of this problem, see fig. 3. By linearization of the Si-function as approximation one obtaines a function between the shock-rise-time T and the limiting frequency f_1

$$f_1 = 1/2T \qquad (5)$$

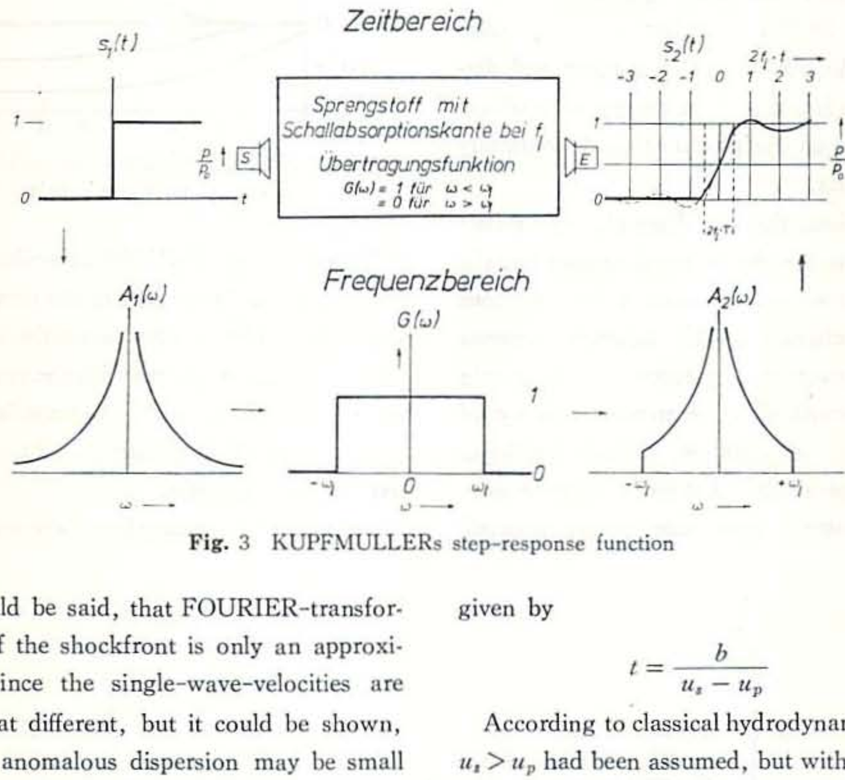

Fig. 3 KUPFMULLERs step-response function

It should be said, that FOURIER-transformation of the shockfront is only an approximation since the single-wave-velocities are some what different, but it could be shown, that the anomalous dispersion may be small for the case discussed here.

Now it is possible to connect the shock-rise-time with an ultimate frequency f_1 taking into account the experimental HUGONIOT-equation of the unreacted explosive. Considering this and the above results the problem is to be treated in the hydrodynamical way. According to this the classical duration of a particle in the shock-zone of the length b is given by

$$t = \frac{b}{u_s - u_p} \qquad (6)$$

According to classical hydrodynamics always $u_s > u_p$ had been assumed, but with the results of fig. 1 this isn't true in general for discontinuities in amatrix. Since the maximum particle-velocity of a cavity ($\rho' = 0$) is

$$u_p' = 3u_p \qquad (7)$$

t becomes infinity for the cace

$$u_s = 3u_p \qquad (8)$$

according to equation (6). If this condition is realized by shock-attack a bubble may have an infinite duration in the shock-zone. If the

u_s/u_p-ratio is diminished the imaginary part of SKUDRZYK-solution is different from zero, the zero-density-discontinuities show high acoustic power and act as hot-spots in the shock-zone. Moreover they cause a steepening-up of the shock-front.

Since there are numerous experimental values about shock-initiation of liquid and solid explosives available the statement above may be proved. For details see original paper. In fig. 4 it is shown that no detonation is obtained only in liquid explosives in the case of

$$u_s/u_p > 3 \qquad (9)$$

but for

$$u_s/u_p < 3 \qquad (10)$$

detonation mostly occurs. The induction-time between the energizing shock and the detonation gets very high for the case

$$u_s/u_p = 3 \qquad (11)$$

This is also to be expected according to this model since the interaction according COLE-circle tends towards zero. For obtaining a detonation a small excessive amount of

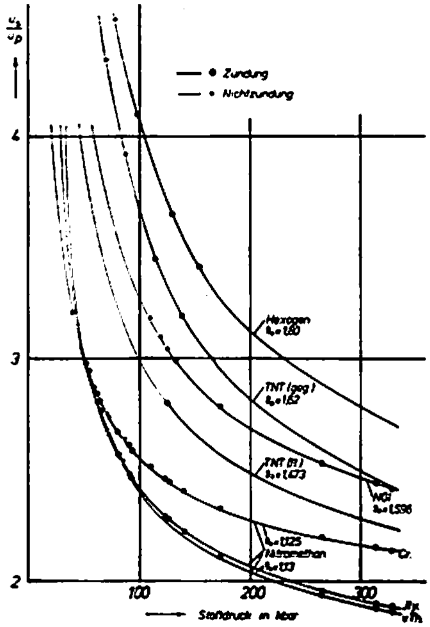

Fig. 4 Test of the initiation-model for liquid and solid explosives

the particle-velocity of the discontinuity u'_p in respect to u_s is necessary.

These conditions don't hold, however, for solid and crystalline explosives. The reason of this is discussed below.

For numeric calculations of the conditions of initiation of liquid explosives, the value of viscosity to be inserted into equation (2) is still unknown. It should be decided whether the normal viscosity or any high-pressure/high-temperature value should be taken. To decide this experimental facts are available. Dempster[2] and Avogadro[3] made experiments dealing with sensibilization of blasting-gelatine by adding dense, finely devided inert particles with a density-ratio $\rho'/\rho_\infty > 2$ to it. Also an optimum particle-diameter in the range of about $5/u$ had been found.

This sensibilization is not realized by classical approach. It may be conceivable by this model in the following way.

In order to be recognized as sensitizers the particles have to interact with the blating-gelatine. If it is assumed that this interaction tends to a maximum, which shows to be not exactly correct as shown later, a corresponding ROTH's number as a function of density-ratio is obtained. Inserting the particle-radius the value of viscosity is obtained. For a wide variety of energizing shock-pressures the normal viscosity of nitroglycerine is obtained within tht limits of accuracy. It had been surprising that the Nitrocelulose didn't affect the value. But this possibility is wellknown from the results of the drag-reducers[4], the chains are cracked by the rapid motion of the particles, furthermore only 6% by weight of NC are present. As the time of rotation of a nitroglycerine-molecule is comparable to the rise-time of the shock, the viscosity isn't changed.

According to the COLE-circle the sensitizers bring real losses to the system in the shock-front whereas the cavities bring negative losses, which represent gains. For some conditions the gains of the cavities are exceeding the losses of the dense discontinuities. Carrying heavy particles away from shock-front cavities are created by reasons of continuity, causing a gain to the shock-front.

The real possible loss is experimentally realized since Sensitized explosives detonate well only by strong initiation. By weak initiation no detonation occures, or if so, detonations don't continue. Latter is never realized by explosives sensitized by bubbles. According to this the sensibilization is a secondary effeect, producing smaller losses for acchieving an overcompensation by cavity-gains.

This and also the newer results about the initiation of "homogeneous" explosives give strong indications that a cavity-formation is necessary before detonation occurs in general. The experimentally established shock-opacity before onset of detonation may be the consequence of cavitation and bubble-formation. But it should be noticed, that this picture isn't accepted by everyone up to now. Assuming the validity of this assumption the radius of the created bubbles formed by cavitation may be calculated. ROTH's number as function of the initiating pressure may be calculated from the experimental HUGONIOT-equations of liquid explosives. Inserting the known viscosities in the expression for Ω gives the radius of the assumed bubbles as function of energizing shock-pressure. The results for some liquid explosives are shown fig. 5.

It is to be noticed that the bubbles according to this calculation show the same order of magnitude as those determined in experiments by Erlich, Wooten and Crewdson[5] for shocked glycerol.

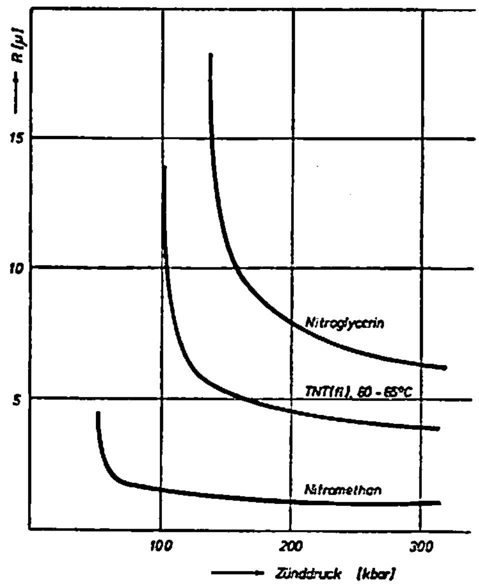

Fig. 5 Calculated radius of cavities in liquid explosives as function of energizing pressure

As it is seen in fig. 5 the cavity-radius is increasing with decreasing shock-pressures. It may be reasonable that cavity-growth is further continued below the pol $u_s = 3u_p$.

For bubbles comparable to the shock-rise-length the outlined model according to the SKUDRZYK-solution is failing. With increasing R Ω goes to infinity and no interaction is possible.

If

$$u_s = A + Bu_p \qquad (12)$$

is the Hugoniot-equation, one may see, that for weak shocks in the near acoustical field u_s may tend towards A. Since A is also a pol for the limiting frequency f_1, both lowering of the energizing pressure and increasing the cavity-radius show in the same direction causing no possibility of interaction. Since the f_1-p-function is very steep a detonation should only be obtained below A. Since the low-velocity-detonation (LVD) depends on bubbles, perhaps created by the vibration of the confinement, and also its sound-velocity, one should find

$$D_{LVD} < A \qquad (13)$$

if the sound-velocity of the confinement doesn't differ too much.

In fig. 6 condition (13) for nitroglycerine is shown and the frequencies of experimentally observed detonation-velocities of nitroglycerine are registered.

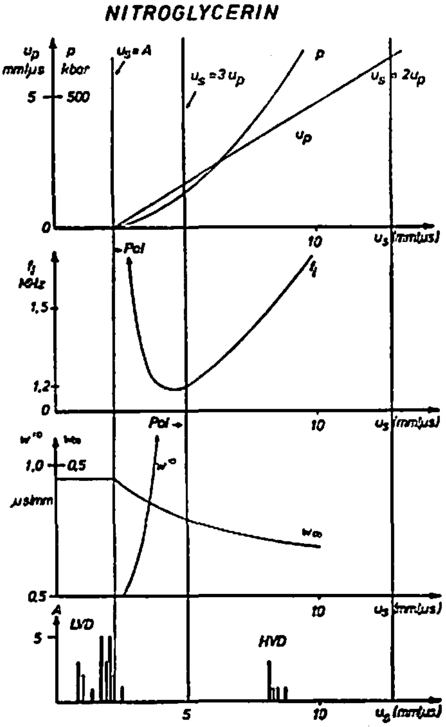

Fig. 6 Calculated quantities for NITROGLYCERIN

As demonstrated the size of the cavities and their variation shows an importance. Therefore this problem is now considered here inview to detonation.

According to the investigations of Kaelble[6] in a viscoelastic medium a stable cavity of radius R^+ is possible. Any other cavity with radius $R \neq R^+$ is unstable.

$$R^+ = \frac{2\gamma}{p^+ - p_{LV}} \qquad (14)$$

γ is the surface tension and

$p^+ - p_{LV}$ the pressure difference between the inside of the cavity and the surrounding medium diminished by the vapour-pressure p_{LV}.

Kaelble calculated the relative bubble-formation energy of an arbitrary cavity in respect to a stable one and obtaines

$$E/E^+ = (R/R^+)^2 - 2(R/R^+)^3 \qquad (15)$$

According to this formula the energy of cavity-formation is maximized for the stable cavity R^+ and lower for any other $R \neq R^+$. This means that if any bubbles are created $R > R^+$ they will expand and contrary to it, if $R < R^+$ they will collapse. The branch of growing and shrinking cavities is divided by an energy-barrier.

If the bubbles are shrinking, high-velocity-detonation is possible, see fig. 5, if, however, they are growing, they have to tend in the branch of no interaction of the outlined manner and Ω tends to infinity additionally. Because the interaction is now limited in following up an other, less efficient mechanism' reaction-products of *LVD* don't correspond to these produced by *HVD*, the reaction isn't completed as experimentally outlined by Cook[7].

Since the stable radius R^+ depends on surface tension and vapour-pressure and ROTH's number is controlled by viscosity, the stability of *LVD* is given by these parameters together with rheological conditions. According to this model a transition from *LVD* to *HVD* and contrary to it should be possible. It had been suggested up to now that only the transition *LVD* to *HVD* should be possible, but according to T. Hikita[8] both transitions had been realized.

The sensitivity to physico-chemical quantities is also established by experiments. For Nitromethane (NM) in pure state only *HVD* seems possible, whereas at 90/10% by weight of NM/Tetranitromethane (TNM) both *HVD* and *LVD* are obtained.

This is to be understood since vapour-pressure and surfacetension of a binary mixture are strongly dependent on little additions of the second partner or impurities thus determining a modified R^{*}. It is now understandable that liquid explosives from the same supplier but in different bottles may show some different initiation-properties[9].

This result is deepened by investigations of Haeuseler[10] on a variety of liquid binary systems concerning their initiation behaviour. But the physico-chemical properties of such systems are still not investigated.

The viscosity had been calculated assuming maximum interaction of the dense particles with the surrounding medium. For cavities causing gains this would be the case for

$$u_s = 2u_p \qquad (16)$$

according to the COLE-circle. Up to now no explosive could be found suffering this upper condition by stable detonation-velocity. If an overdriven detonation should be below this condition, the interaction gets smaller, chemical reaction isn't completed and consequently the detonation-velocity decreases for sustaining the self propagating chemical shock. In practice condition (16) is never realized because of the losses in the system alwas present, see fig. 6.

It is of interest that an analogy of the outlined detonation mechanism is also known in electronics. An acoustic-electrical amplification is possible for the case that the carrier-velocity of electricity overcomes the sound-velocity in the crystal.

The carriers are energizing the sound-wave. But it is not possible to treat the detonation-mechanism according to this WHITE-mechanism[11] since detonation is far from the acoustical case, the bubble-velocity can't be determined by constant injection and the problem isn't to be treated by linearization.

Since the cinematic viscosity of gases is similar to or greater than that of normal fluids, it is not surprising that antiknocking is to be explained in the similar way as the sensitizers. Since in this case the density-ratio is very high, maximum interaction of lead-oxide-particles predominates still at very low velocities and strong attenuation is obtained, see fig. 2 for the case of $\rho'/\rho_\infty \approx 20{,}000$.

This interpretation isn't very enjoyable as antiknocking produced by this mechanism is only possible through heavy particles. These, however, destroy the combustion-engine, or, if not, are poisons like lead-oxide.

Since solid explosives are characterized by large anisotropy of the single crystal properties, a crack velocity in the matrix is possible exceeding the shock-velocity (Steverding and Lehnigk[12]). For wave-length similar to the grain size acoustic absorptions are possible since the wave-front interferes at well localized "hot-spots" on every crystallite resulting from its anisotropy. The first step of initiation by weak stimuli is to be understood in term of fracture mechanics since at low pressures the crack-propagation seems to be the fastest event. Also the pores may interact with the matrix acting like exciting wedges if pore-mobility starts and inter-crystalline crack-formation is sensitized, see COLE-circle starting at, resp. near $u'_p/u_p \approx 1$. If, however,

Fig. 7 Detonating Composition-B-charge in water showing that the zone of light is ahead in respect to shock-front. (I have to thank Dr. Held of Bölkow-Messerschmitt for making available this picture.)

the mobility of the pores is realized, this effect gets the fastest one.

Experimentally this may be seen at the light before the shock-front, in a detonating explosive, see fig. 7. According to the Hugoniot-equation of the explosive and its detonation-velocity of about 8,000 m/s, the velocity of full activated pores reach about $u_p' \approx 9,600$ m/s. The common between both mechanism is, that the duration of a cavity in the shock-zone gets infinity.

References

1) Skudrzyk, E.: The Foundations of Acoustics Springer, Wien, 1971
2) Dempster, P. B.: Disc. Faraday Soc. 22 (1956) 196-202
3) Avogadro, L.: Annali di Chimica 49 (1959) 352-357
4) Patterson, G.K., J.L. Zakin and J.M. Rodriguez: Ind. and Eng. Chem. 61 (1969)$_1$ 22-30
5) Erlich, D.C., D.C. Wooten and R.C. Crewdson: J. appl. phys. 42 (1971)$_{13}$ 5495-5502
6) Kaelble, D. H.: Trans. Soc. Rheol. 15 (1971)$_2$ 275-296
7) Cook, M. A.: The Science of High Explosives, Reinhold Publishing Corp.. New York 1958
8) Hikita, T.: personal communication
9) Campbell, A. W., W. C. Davis and J. R. Travis: Phys. Fluids 4 (1961)$_4$ 498-510
10) Haeuseler, E.: Explosivstoffe 1 (1953)$_{6/7}$ 64-68
11) White, D. L.: J. appl. phys. 33 (1962)$_8$ 2547-2554
12) Steverding, B. and S. H. Lehnigk: Int. J. of Fracture Mech. 8 (1972) 59-73

I) Leider, C. O.: Naturwiss. 55 (1968)$_8$ 384-385
Leiber, C. O.: Beeinflussung der Initiierung durch Diskonti-nuitäten, Vortrag Institut für die Chemie der Treibund Explosivstoffe, Karlsruhe 1970 S. 71-90
Leiber, C. O.: Planseeber. Pulvermetallurgie 18 (1970)$_3$ 178-193
Leiber, C. O.: Planseeber. Pulvermetallurgie 19 (1971)$_1$ 25-36
Just, W., U. Dworak und C. O. Leiber: Planseeber. Pulvermetallurgie 20 (1972)$_3$ 219-232
Leiber, C. O.: Rheol. Acta 11 (1972)$_{3/4}$ 302-312
CTI-Ber. 3. 2-3/3005/72, Rheol. Acta in press
CTI-Ber. 3. 2-3/3053/72, Rheol. Acta in press
CTI-Ber. 3. 2-3/3019/72.