JOURNAL OF MATERIALS SCIENCE 26 (1991) 369–382

Dynamics of spreading of industrial oil-in-water emulsions on steel surfaces

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The spreading of industrial oils, pure and emulsified in water, has been investigated on rough steel surfaces. Oils wet the surface regularly, the spreading remains circular and the contact area can be empirically correlated to time *t* by a power law similar to those of pure homogeneous liquids. Similar laws can also be found for oil-in-water emulsions, but in this case the spreading behaviour is quite different: first it is not circular, irregularities appear depending on the industrial oil; then retractions can occur and eventually, with some emulsions thinning of the central zone may occur after a certain time. All these effects might be due to the actual composition of these oils which are essentially esters of fatty acids dissolved in mineral oils with various added surfactants. This kind of experiment might be a very simple test to aid the choice of an appropriate rolling-oil.

1. Introduction

Steel manufacturing is one of the industries where the wetting phenomenon is becoming increasingly important. To meet the productivity and the market requirements especially for car makers, manufacturers have to produce faster and faster, tougher, thinner and cleaner steel strips with consistent and maintained texture to aid further treatment as paint adhesion and press performance. This is achieved in the cold roll mills, with the "proper" rolling oil.

Rolling oils are generally mixed with permuted water at a concentration as low as possible, generally at 2%, to form an oil-in-water emulsion: the water cools whilst the oil lubricates. The oil is efficient if among other things it is able to plate-out and adhere to the roll and strip surfaces as a strongly adherent film of constant thickness, preventing excessive wear, or eventual welding. This is the basic motivation of the present study of spreading of industrial emulsions on steel surfaces.

There have been recently a large number of theoretical and experimental studies on the dynamics of wetting of liquids on solid surfaces due to problems encountered in industrial processes; some progress has been made on pure systems, essentially with pure liquids or liquids containing surfactants or occasional impurities on well defined surfaces [1–5]. Some theoretical predictions could be worked out which are fairly verified by experiments.

As far as we know no study concerning spreading of emulsions has been made on any surfaces: glass, silicon wafer or steel etc..., smooth or rough. This is a far more puzzling system than the previous ones since emulsions are made of several constituents which have different wetting properties and contain surface-active substances which modify the energy level of the substrate during the experiment.

A good spreading of the emulsions and a stable long time behaviour of the deposited film are, however, necessary for the quality of the rolling oil. Hence the purpose of this paper is two-fold: it sheds some light on the dynamics of spreading of industrial oils and their emulsions in water and it proposes a very simple test which could be a valuable addition to the list of rolling oils homologation tests.

The paper is arranged as follows. The experimental procedure and tests with well known materials are first described then a series of experiments are carried out in order to show the effect of known surfactants on spreading: nitroethane saturated with water is spread first pure, then added successively with anionic, non-ionic or cationic known surfactants. Eventually the spreading of industrial oils and emulsions are observed. Emulsion spreadings show some irregularities, sometimes retractions may even occur.

Finally a discussion is presented which attempts to explain the non-circular spreading, thinning of the central zone and retractions. With emulsions, however, in spite of these wetting irregularities, during most of the spreading, the measured liquid–solid contact area *A* can be empirically correlated as a function of time, *t*, by power laws similar to those found for homogeneous pure liquids [6].

2. Experimental procedures

A good reproducibility in wetting experiments can only be achieved if rigorous experimental procedures are strictly defined.

2.1. Liquids

The actual compositions of industrial oils are unknown, but they contain essentially esters of fatty

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TABLE I Physical constants of liquids: γ surface tension, ρ density, μ viscosity, T experimental temperature

Liquid	γ ($\mathrm{mN\,m^{-1}}$)	ρ ($\mathrm{kg\,m^{-3}}$)	μ (Pa sec)	T (°C)
B	32.5	875	0.200	22
S	29.3	876	0.035–0.039	22
T	30	840	0.039	45
Silicone oil		973	1.000	22
Emulsions				
B 3%		~ 1000	1.5×10^{-3}	22
B 1%		1000	1.3×10^{-3}	22
S 3%		1000	1.5×10^{-3}	22
S 1%		1000	1.3×10^{-3}	22
Pure nitroethane	32.3	1040	0.0006	22
+ Tween	31.7	1040	–	22
+ DTAB	32.5	1040	–	22

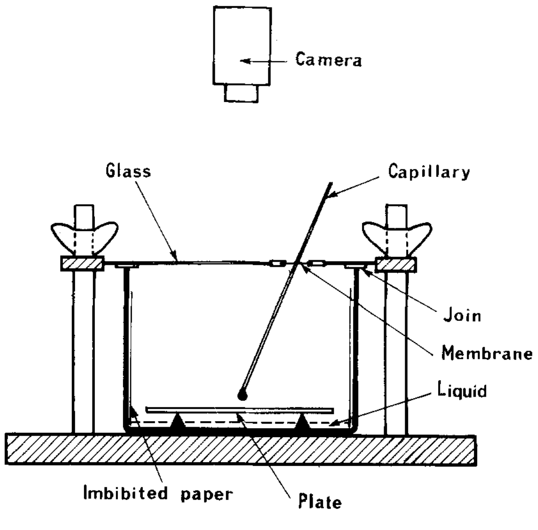

Figure 1 Tight closed cell.

acids dissolved in mineral oil where various surfactants are added in order to stabilize oil–water emulsions.

Three industrial oils B, S and T are used; their physical constants are reported in Table I. Emulsions are made by mixing oils with pure water. Concentrations C are defined as the ratio between the mass of oil and the mass of water. The mixture is shaken for half an hour before each experiment.

Except for industrial oils, liquids used either for spreading, or for cleaning, are pro-analysis quality. Only pure water is used.

2.2. Plates

Metal plates are cleaned by the following procedure:

(a) removing grease with trichloro-ethylene for 10 min in ultrasonic bath,

(b) cleaning with acetone for 10 min in ultrasonic bath,

(c) storage in vacuum if necessary,

(d) dipping in hydrochloric acid for 90 sec,

(e) rinsing with hot water, then pure water,

(f) drying with nitrogen or in a desiccator,

(g) immediate use.

All the rough metal samples (roughness after cleaning procedure is $r_a \simeq 1.3\ \mu\mathrm{m}$) are used once. The smooth surfaces were obtained from the raw metal plates, they had first been cleaned (steps a and b of the procedure), then polished with various grades of silicon carbide paper (200 to 800), avoiding diamond pastes which contain uncontrolled surfactants. The polished samples were cleaned again following steps b, e, f and g of the procedure.

For the glass slides the same cleaning procedure is used, step *d* being replaced by dipping in sulphochromic acid at room temperature. To remove the size parameter [7], all plates used here are square ($5 \times 5\ \mathrm{cm}^2$), the drops being deposited just in the centre.

2.3. Atmosphere and temperature

Except if otherwise mentioned, all the experiments were carried out in a saturated atmosphere in a tight closed cell (Fig. 1). Saturation is achieved by depositing a thick layer of the spreading liquid on the bottom of the cell, the vertical wall being lined with porous paper imbibited by the liquid. Experiments were carried out at room temperature measured with a thermocouple inside the cell; it remained constant at about 22 °C for each run. The drying with nitrogen cools the plate and 15 min are then necessary to regain thermal equilibrium of the whole system. Experiments with oil T were carried out at 45 °C.

2.4. Experimental procedure

Drops are formed at the tip of a fine capillary connected to a constant volume syringe and carefully deposited just on the plate surface. Their volume is equal to 2 µl for all the experiments, however the different wetting properties of the various liquids with respect to the nature of the capillary may induce some discrepancies between the actual deposited volumes, but the error is less than 5%.

All the experiments were carried out inside the cell on horizontal plates (Fig. 1). For each case they were repeated several times. The drop evolution was observed with a CCD camera and recorded on a tape continuously or at regularly spaced times. Images were then numerically digitized and treated with a software specially adapted by ourselves. Areas were measured at each selected time. If the same criteria are used for each experiment, a good accuracy (± 2%) is obtained for the measurement of the areas.

3. Results

3.1. Spreading on smooth surfaces

3.1.1. Spreading on glass

We have first checked our procedure and measurement method by spreading silicone oil of viscosity 1 Pa. sec on smooth float glass and by comparing the results of the literature. The laws for spreading on smooth surfaces are well known [8, 9]

(i) for large drops gravity is the driving force

$$A(t) \propto t^{0.25}$$

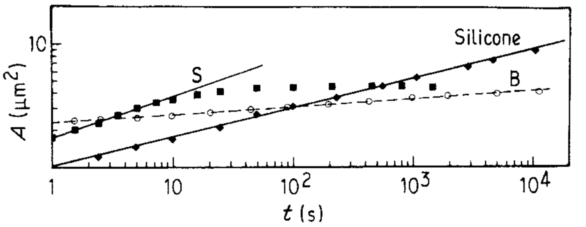

Figure 2 Oils spreading on smooth glass (■ S, ◆ silicone, ○ B).

(ii) for small drops capillary forces cause the spreading

$$A(t) \propto t^{0.2}$$

in both cases viscosity retards the motion.

The transition between the two regimes is related to the radius of curvature R of the droplet compared to the capillary length $l = (\gamma/\rho g)^{1/2}$. In our case, with silicone oil ($l \simeq 2$ mm) a droplet of 2 μl, which is an intermediate volume, gives $R \simeq 1$ mm. Results are plotted on Fig. 2. The exponent α of the spreading law is 0.22 which is very close to the values measured by others [3, 5, 10] and is an intermediate value between the above exponents as could have been expected.

Industrial pure oils spreads regularly, however, the results differ significantly. The B-oil hardly spread on glass ($\alpha \simeq 0.05$) while the spreading exponent of S-oil is larger ($\alpha \simeq 0.32$) but comparable with the usual values of the literature [3] for about 10 sec; after 100 sec it does not spread any longer, it might even retract very slightly. The difference in behaviour is likely to be due to the liquids and the various additives of the oils.

3.1.2. *Spreading on steel*

On polished steel plates (see further, Fig. 7), three phases are observed with B-oil

(i) The droplet spreading is first a power law; the value of the exponent 0.26 agrees fairly well with the predicted value 0.25 on smooth surfaces in the gravity viscous regime [8].

(ii) The droplet then stops spreading for about 200 sec.

(iii) In the last phase, spreading starts again with a power law whose exponent is about 0.16 which is a little less than the predicted value 0.20 of the capillary regime.

This unusual behaviour is not encountered with simple liquids, it is probably due to some chemical hysteresis effect due to slow migration of surfactants ahead of the film which changes the value of the spreading coefficient.

3.2. Spreading on rough surfaces

3.2.1. *General*

Three main steps can be distinguished during spreading on rough surfaces, their existence and duration depend on the characteristics of the liquids and of the surfaces.

3.2.1.1. First step: $0 < t < t^*$. During this step (Fig. 3a) the gravity causes the spreading which is retarded by the liquid viscous stresses. An apparent macroscopic contact angle subsists. The thickness of the droplets is much larger than the plate roughness. The liquid–solid contact area is related to time by a power law with exponent α_1

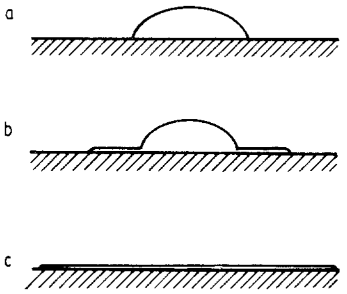

Figure 3 Different steps during droplet spreading.

$$A(t) \propto t^{\alpha_1}$$

3.2.1.2. Second step: $t^* < t < t^{**}$. During this step (Fig. 3b) a liquid ring forms around the droplet central cap which acts as a reservoir. The ring spreads at the expense of the cap in a way which is strongly liquid dependent, but, in most cases, its edge penetrates inside the roughness of the plate as a liquid invades a porous medium. Power laws with different exponent values are obtained for the evolution of the film area $A(t)$ and of the ring radius $\Delta R(t)$. $A(t)$ is still proportional to t^{α_2} with α_2 different from α_1.

3.2.1.3. Third step: $t > t^{**}$. During this step (Fig. 3c) the central cap vanishes and the droplet still spreads with a power law

$$A(t) \propto t^{\alpha_3}$$

for the systems considered in this paper the exponent α_3 is found equal to α_2 and t^{**} cannot be evaluated.

3.2.2. *Spreading of industrial oils on steel plates*

The dynamics of spreading of silicone and industrial rolling oils on steel plates exhibits the three previous steps. The shape of the droplets remains regular and circular (Fig. 4); results, $A = f(t)$, are plotted on Fig. 5.

For industrial oils only, the transition between the first and the second step may be very abrupt (S and T oils) while it is smooth with the silicone and B oils as it has been also observed [11] on depolished glass.

In the first step we could expect the same value of the exponent α_1 as the predicted one ($\simeq 0.25$) for smooth plates in the gravity viscous regime since the roughness of the steel plates is much smaller than the droplet thickness. Actually the measured exponent is slightly higher for S- and T-industrial oils and quite comparable for silicone oil and B-oil (Table II). The precision of the measurements is quite good, the slight discrepancy in the value of the exponent means that the similarity solution obtained by Lopez *et al.* [8] for smooth surfaces under-estimates the rate of spreading in the present case.

In the second step the exponents α_2 are ranging between 0.65 and 0.77. The transition time t^* depends

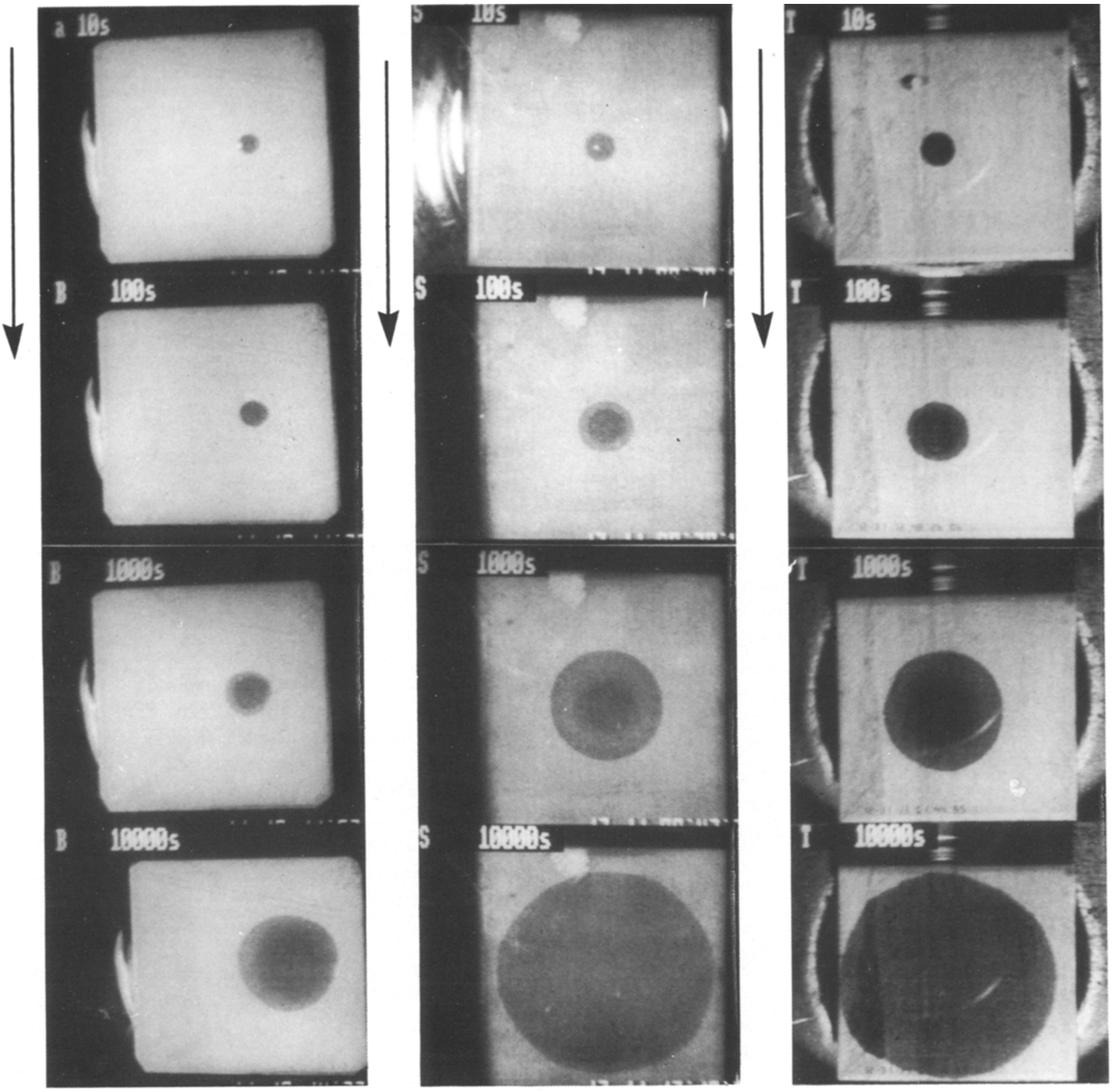

Figure 4 Photographs, at several times, of industrial oils spreading on rough steel.

on the viscosity with a law in $\mu^{3/2}$ (Fig. 6) while, at the transition, the mean thickness of the layer $h^* = V/A^*$ (A^*: is the area of the droplet of volume V at $t = t^*$), is quite constant for similar plates (Table II), which means that the driving force is then constant. The transition thickness changes with the plate surface properties since the driving force of capillary origin [11] is essentially dependent on the solid surface energy.

TABLE II Spreading characteristics of non emulsified oils: t^*: transition time; $h^* = V/A^*$, (V droplet volume, A^* area at t^*); α_1 and α_2: exponents of the spreading power law during first and second steps

Oils	t^* (sec)	h^* (μm)	α_1	α_2
Silicone	3500	36	0.29	0.65
B	370	33	0.27	0.66
S	60	29	0.34	0.66
T	130	34	0.36	0.77
B with water saturated atmosphere	6500	10.9	0.31	0.87
B on polished steel	280	24.3	0.26	0.16

Indeed in a water saturated atmosphere (Fig. 5, dashed lines) the transition occurs much later than in dry atmosphere, while the exponent α_1 of the power law is essentially the same. The thickness h^* is then somewhat lower than in dry spreading. In a saturated atmosphere there is clearly water adsorption on the solid plate, and the liquid is actually spreading on water molecules. The influence of surface roughness has also been tested with B-oil (Fig. 7). On polished steel plate, α_1 is quite near the predicted value [8], while α_2 is clearly lower. On rough surfaces the exponents are higher especially α_2 which is four times the measured value on the polished plate.

Dipping the steel plate in hydrochloric acid for 10 min instead of 1 min does not change much the oil

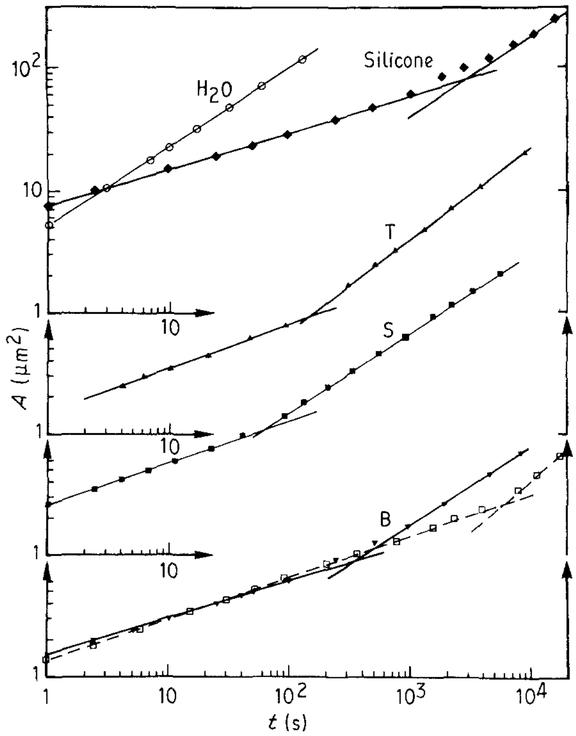

Figure 5 Spreading of oils on rough steel: droplet area plotted against time (○ H_2O, ◆ silicone, ▲ T, ■ S, ▼ B, □ water saturated atmosphere).

spreading law: the exponent of the first regime is slightly increased, hence, the transition time t^* occurs a little earlier while the droplet thickness h^* at this time t^* is a little smaller. The second exponent is the same as before.

3.2.3. *Effects of surfactants*

The effects of various surfactants on the spreading of liquids on raw sheet metal surfaces were investigated. Anionic (SDS), cationic (DTAB) and non-ionic (Tween 20) surfactants are successively dissolved in nitroethane saturated with water; concentrations being respectively 3.6×10^{-2}, 3.8×10^{-2} and 1.5×10^{-2} $\text{mol}\,\text{l}^{-1}$. The experiments were performed in dry or saturated atmosphere. In both cases the spreading droplet remained circular.

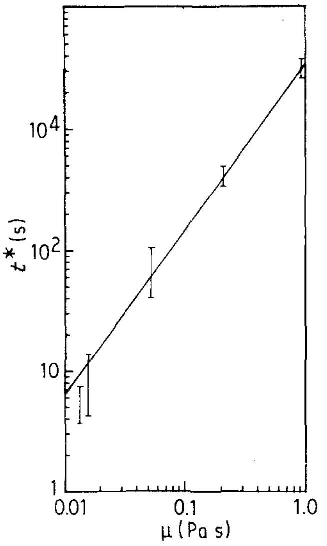

Figure 6 Evolution of the transition time t^* as function of the dynamic viscosity of the liquid when droplets are spread on rough steel.

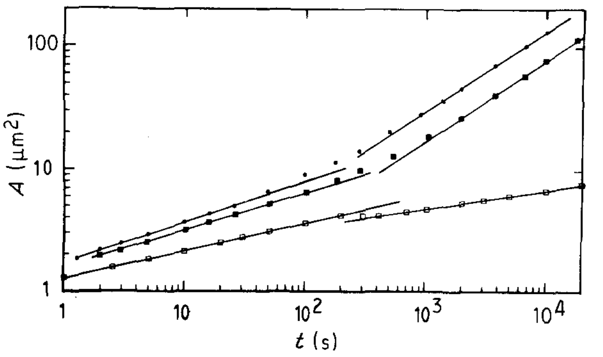

Figure 7 Influence of the roughness: spreading of B-oil on steel (□ slope 0.26, 0.16) polished; dipped 1′ (■, slope 0.30, 0.64) and 10′ (●, slope 0.36, 0.66) in hydrochloric acid.

3.2.3.1. Dry spreading. When spreading occurs in a dry atmosphere the edge of the drop is always well defined (Fig. 8). With Tween and DTAB, the drop spreads until a maximum area is reached (Figs 8 and 9), then the central cap continues to drain away and finally it remains only a very thin film with a slightly thicker ring around it. On the other hand with the anionic surfactant SDS, after reaching a maximum area, the drop diminishes and finally vanishes entirely; no deposit remains on the surface.

3.2.3.2. Spreading in a saturated atmosphere. In a saturated atmosphere a fairly thin film is formed on the plate. The drop then spreads very quickly because the liquid is spreading on itself with no autophobic effect. The cap is immediately surrounded by a rim. With pure nitroethane the outside of the rim is fairly diffuse, its border line cannot be exactly defined and no measurement is possible. The same phenomenon occurs when nitroethane is added with Tween 20 (Fig. 10b). If, however, nitroethane is added with SDS or DTAB (Fig. 10a and c) the contact areas can be evaluated and the value of α measured (Fig. 11). In these two cases, after a time t_f, the spreading stops. This time t_f is much shorter with DTAB (30 sec) than with SDS (1500 sec), and the final area is smaller for DTAB than for SDS. Marmur [3] and Marmur and Lelah [12] have already observed such behaviour with aqueous surfactant solutions on glass: adsorption of cationic proceeds faster than anionic or non-ionic surfactants. This is a similar result to the one obtained by Bisio *et al.* [13] who observed that the cationic surfactants adsorb vertically at the surface while the anionic or non-ionic surfactants adsorb horizontally.

Finally, for the two cases; dry or saturated atmosphere spreading, if the plates are exposed to the ambient atmosphere, for a long time (several days) a rusty stain appears where the DTAB has spread. In contrast for the two other kinds of surfactant no iron stain appears. Cationic surfactants thus adsorb at the sheet steel surface and, unlike what happens on glass, it makes the plate hydrophilic. The adsorption is

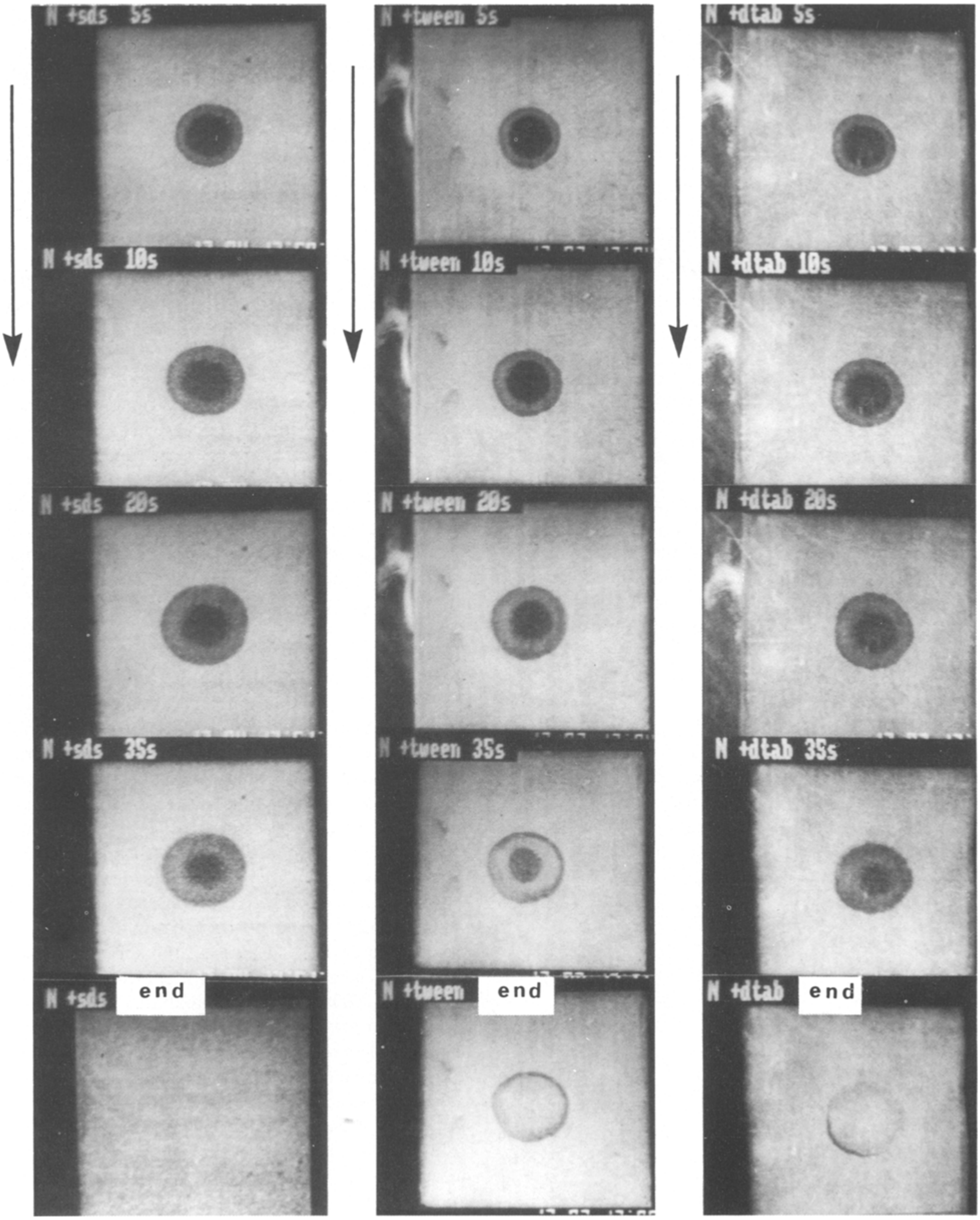

Figure 8 Photographs, at several times, of nitroethane doped with surfactants, spreading on rough steel: dry spreading.

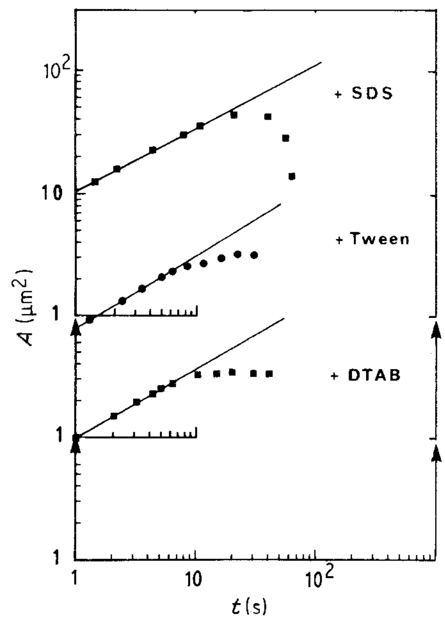

Figure 9 Spreading of droplets of nitroethane doped with surfactants: dry spreading.

probably due to the same phenomenon as that observed by Damiana and Bosë [14]: cleaning with chromic acid induces negative charges on glass, so cationics are attracted and anionics pulled away; with sheet steel, chlorhydric acid dipping would have the same effect.

3.3. Emulsion spreading

Unless otherwise mentioned all the experiments are carried out in a saturated atmosphere to avoid evaporation effects. The spreadings of emulsions at low oil concentration differs considerably from pure oils.

3.3.1 B-emulsions

For the concentrations 1 and 3% of B-oil emulsion, two main steps can be observed:

(1) The spreading is first irregular in direction (Figs 12 and 13); the liquid invades the plate as a liquid imbibes a porous medium (Haines jump). At the centre of the drop the cap remains first unchanged and forms a sharp contact angle with a very thin foot that spreads around it.

(2) After a time $t_{\max}$ (Fig. 14) the foot retracts and vanishes progressively until just the cap remains. At that moment, the cap also spreads irregularly and produces a final drop of quasi uniform thickness but with a much smaller area than the one reached at $t_{\max}$.

After contact with the ambient atmosphere, rust appears first on places which have not been covered by the emulsion later, then on the surface covered before retraction, but never on the central spot.

3.3.2. S-emulsions

For S-emulsions spreading proceeds differently with the concentrations $c = 1$, 2 and 3% (Figs 15 and 16).

With $c = 1\%$ (Fig. 17), as with B-emulsions, retraction occurs then the cap spreads and after about 6000 sec a uniform film is obtained. Spreading does not stop at this time; progressively the cap drains off just after retraction. After 7000 sec a clearer area at the location of the initial central cap appears together with a darker ring around it which remains indefinitely.

With $c = 2\%$, retraction does not occur, the liquid inside the cap drains progressively out and after about 2000 sec, the central zone becomes poorly defined and clearer.

With $c = 3\%$, the behaviour is quite similar to that with $c = 2\%$ the α exponent is greater and transition time t^* is shorter; the process is faster.

3.3.3. T-emulsions

The spreading of T-emulsions is much more regular and the droplets remain quasicircular (Figs 18 and 19). For the same concentration i.e. 3%, the exponents α are smaller than for B and S-emulsions, 0.27 and 0.43 instead of 0.3 and $\simeq 0.6$, respectively, (cf. Figs 14 and 16), when t^* is longer. Later, however, after 250 sec, for example, the droplet area remains smaller: only 1/10th of the other ones. Nevertheless, experiments must be carried out at 45 °C, as was stated in Section 2.3. The cell was only placed on a heating plate, not in an isothermal room. Thus inside the cell, the temperature may not be exactly uniform and it is possible that weak evaporation is produced near the surface when spreading occurs.

4. Discussion

Emulsions are basically made of three constituents: water which is highly polar, a mixture of naphthenic mineral oil and fatty acid esters which is non-polar, and various surfactants and additives. The nature of the constituents depends on the company and ensures the rolling quality.

In contact with steel the emulsion is usually broken [15] and *a priori* any further evolution may occur depending on what is spreading first. Water may spread on steel as long as it is not made hydrophobic by surfactant adsorption which in turn favours oil spreading.

Three main points should be discussed: non-circular shape and retraction of the drops with B and S-emulsions, and thinning of the central part of S-emulsion drop.

4.1. Non-circular shapes of the drop

The non-regular shape of the droplet which is observed with B and S-emulsions at low concentrations could have various origins:

(i) the physicochemical heterogeneities of the plates,

(ii) the plate roughness,

(iii) the breakdown of the emulsion and the separation of the two phases,

(iv) a Marangoni effect.

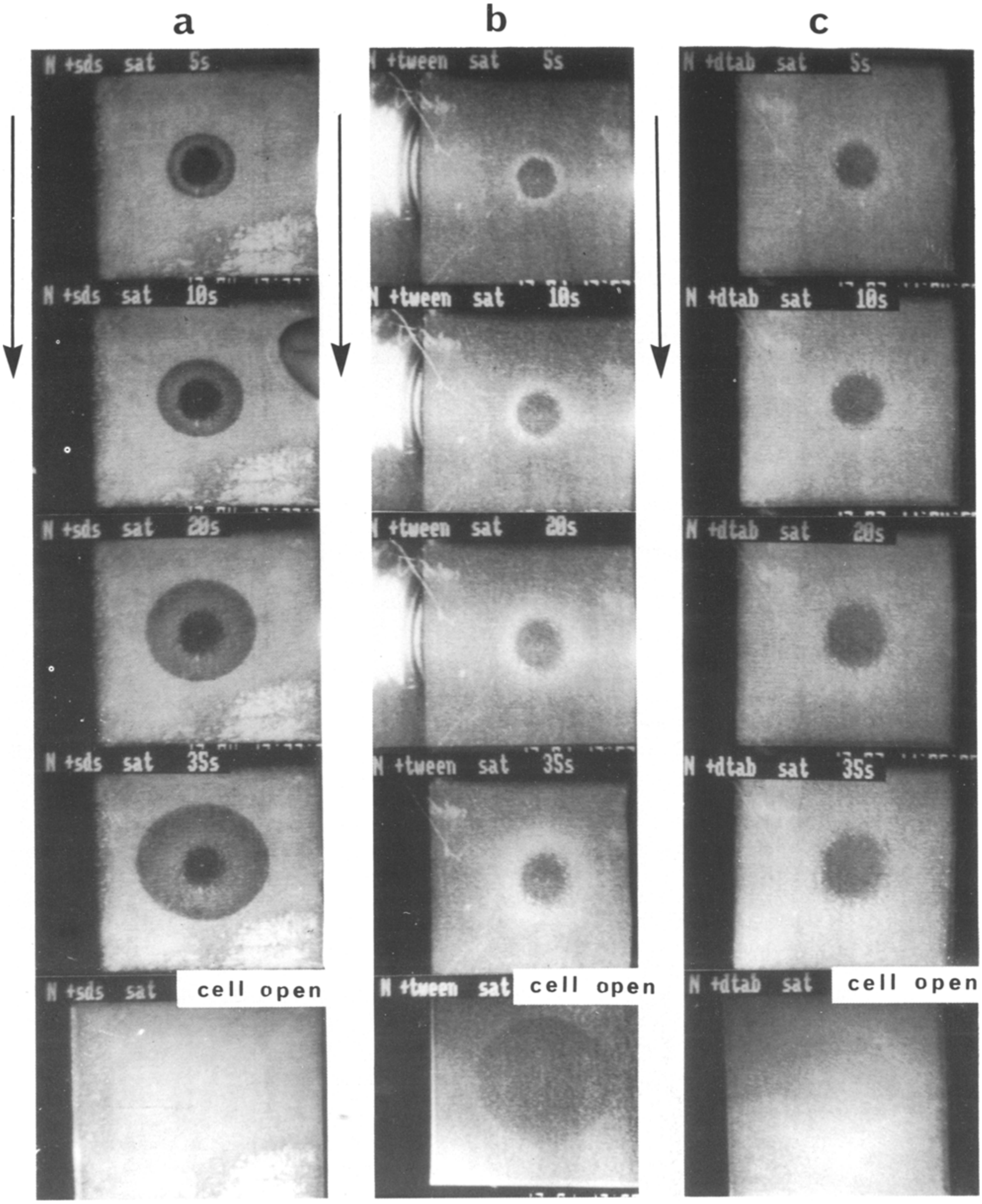

Figure 10 Photographs, at several times, of droplets of nitroethane doped with surfactants, spreading on rough steel: saturated atmosphere.

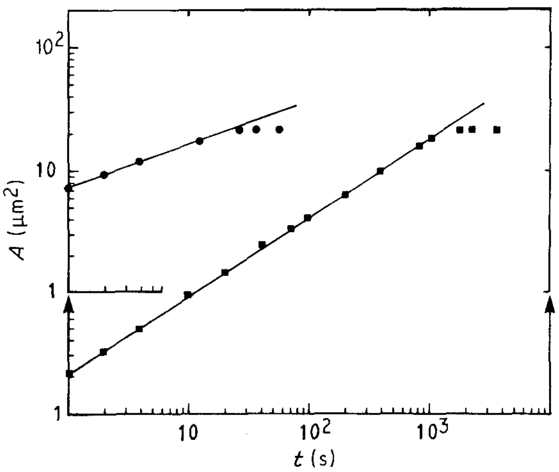

Figure 11 Spreading of droplets of nitroethane doped with DTAB (●, slope 0.35) and with SDS (■, slope = 0.63): saturated atmosphere.

The very rigorous cleaning procedure should *a priori* avoid different physicochemical properties on some particular area of the plates. Indeed, no irregularities were observed with non-emulsified liquids or surfactant solutions.

The roughness can only have an influence if its size is comparable with the thickness of the droplet, more exactly, of its foot in the present case. It does explain the "Haines jumps" type progression of the liquid front in case of B-emulsion ($c = 3\%$), but this effect should occur all around the droplet. On Fig. 13, it is observed that, in the first step, the droplet does not spread on one side and that a foot is developed on the other side; a cap remains at the centre of the drop and makes a very visible contact angle with the foot. This effect looks like an instability: the primary film has probably brought the surfactant ahead of the foot which adsorbs locally on the steel preventing water spreading on this side, and which favours oil spreading on the other side: the separation of the two phases after adsorption of the surfactant inducing local depletion makes this mechanism plausible.

The adsorption of surfactants (favouring oil spreading) just ahead of the foot, induces depletion of the interface which generates a surface tension gradient. In order to restore a uniform surfactant distribution, interfacial convection begins and brings more and more oil and surfactants ahead of the foot; this Marangoni effect induces the direction of spreading. When the maximum area is reached the thickness of the film is very small, about a few micrometres. It is probably even smaller since the film thickness is calculated on the basis of a uniform layer on the plate, which is not the present case because of the remaining

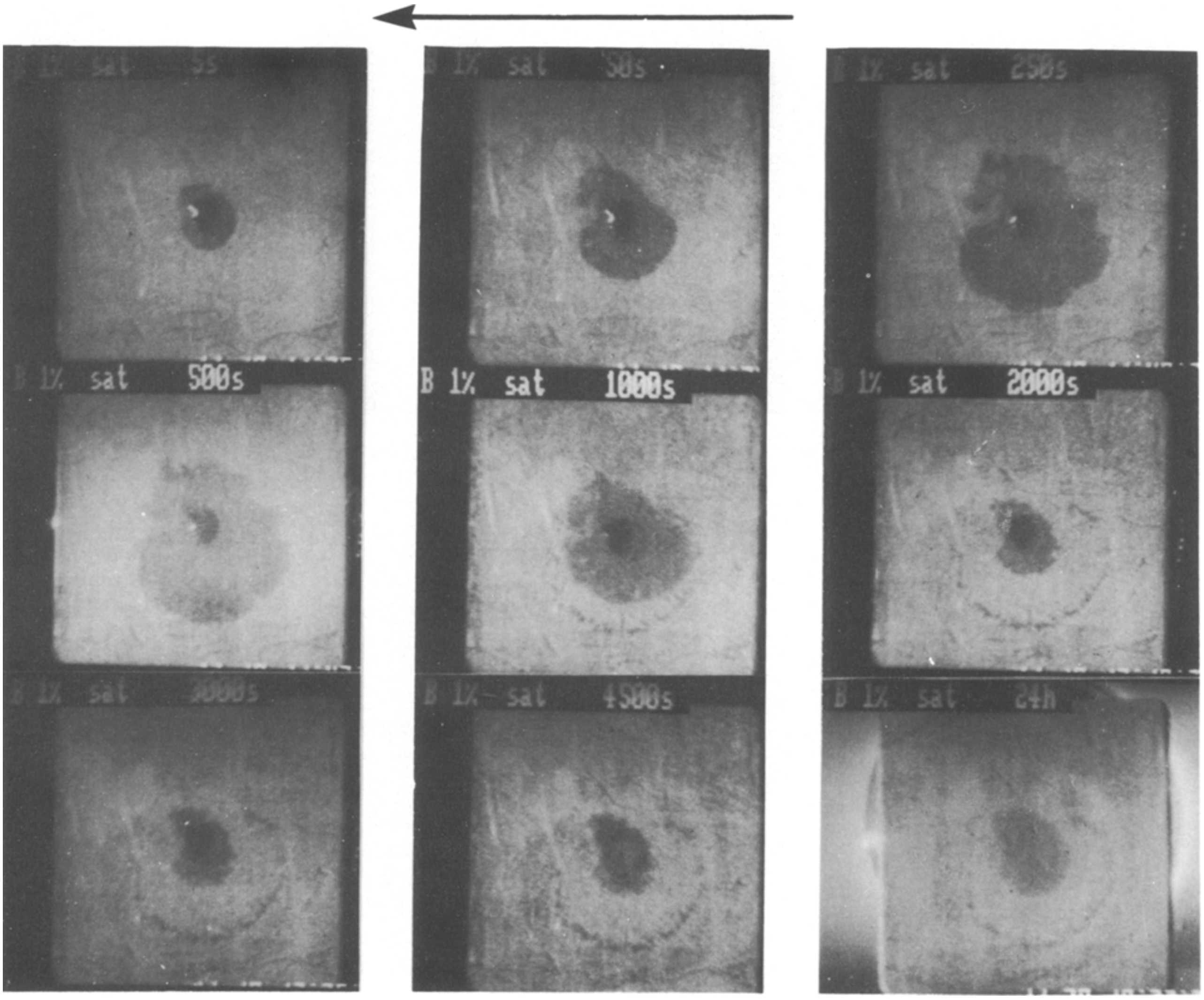

Figure 12 Photographs, at several times, of droplets of 1% B-emulsion spreading on rough steel.

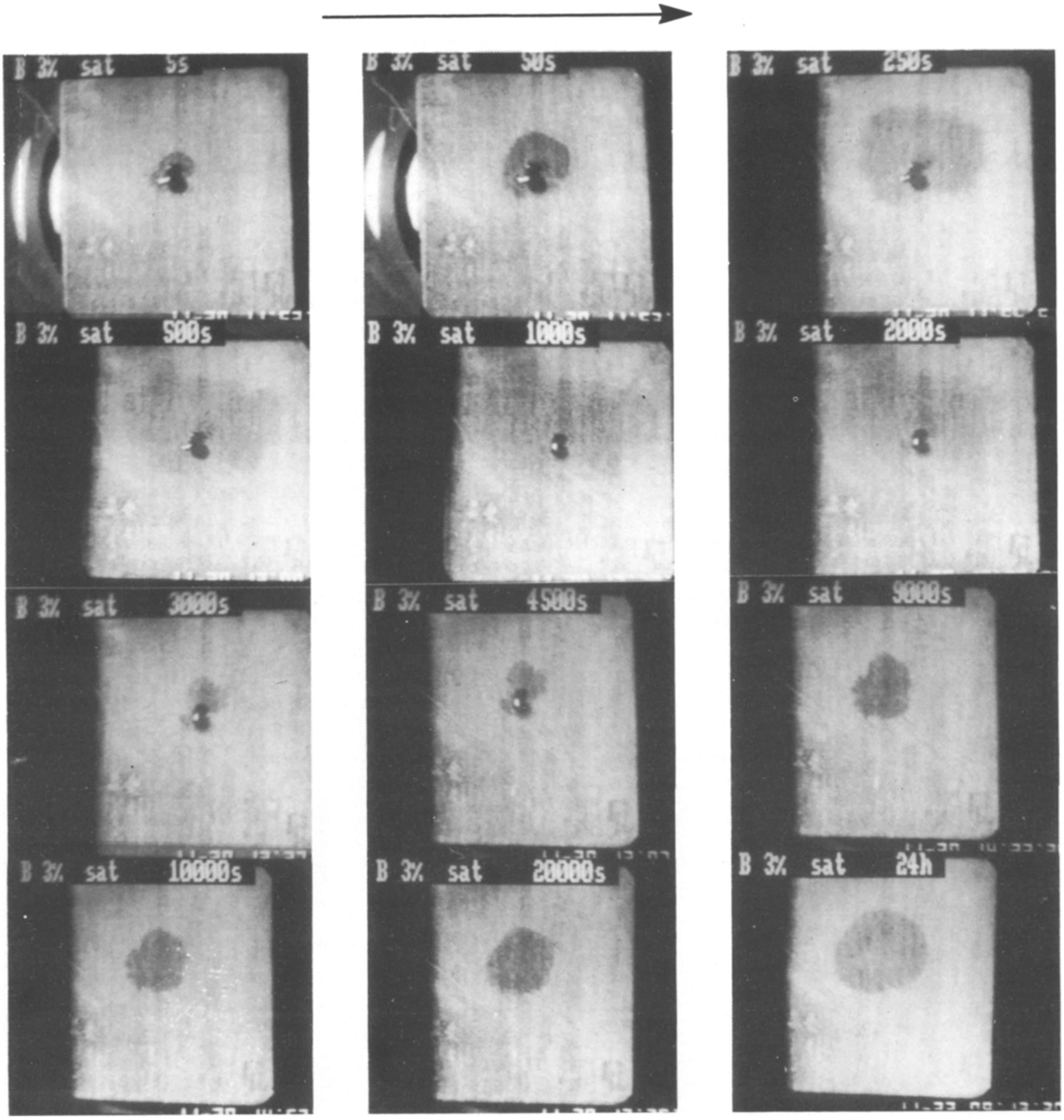

Figure 13 Photographs, at several times, of droplets of 3% B-emulsion spreading on rough steel.

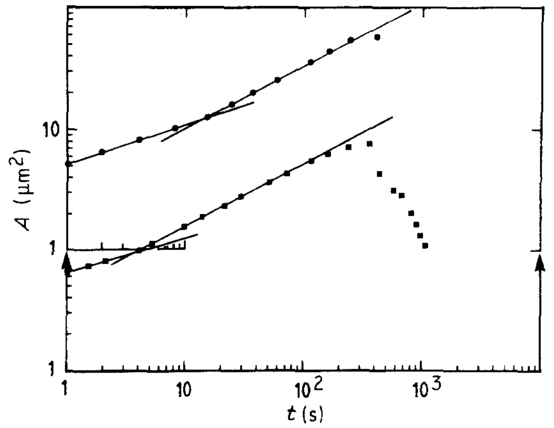

Figure 14 Spreading of B-emulsions: droplet area plotted against time (● 3%, slope = 0.32, 0.53, ■ 1%, slope = 0.31, 0.51).

cap. Spreading can stop because of an excessive viscous dissipation in the foot or because the thickness of the foot is smaller than the roughness [16].

4.2. Film retraction

With B-emulsions and 1% S-emulsion there is retraction of the film. This effect has been observed by Marmur and Lelah [12] and Cottington *et al.* [17] with surfactant solutions. Once the first spreading has occurred, the surface energy of the steel is completely changed from a high to a low level: which means that its critical surface tension γ_c [1] is changed and it is probably very near the surface tension of the spreading liquid. As long as the spreading occurred the contact angle between the foot and the plate was

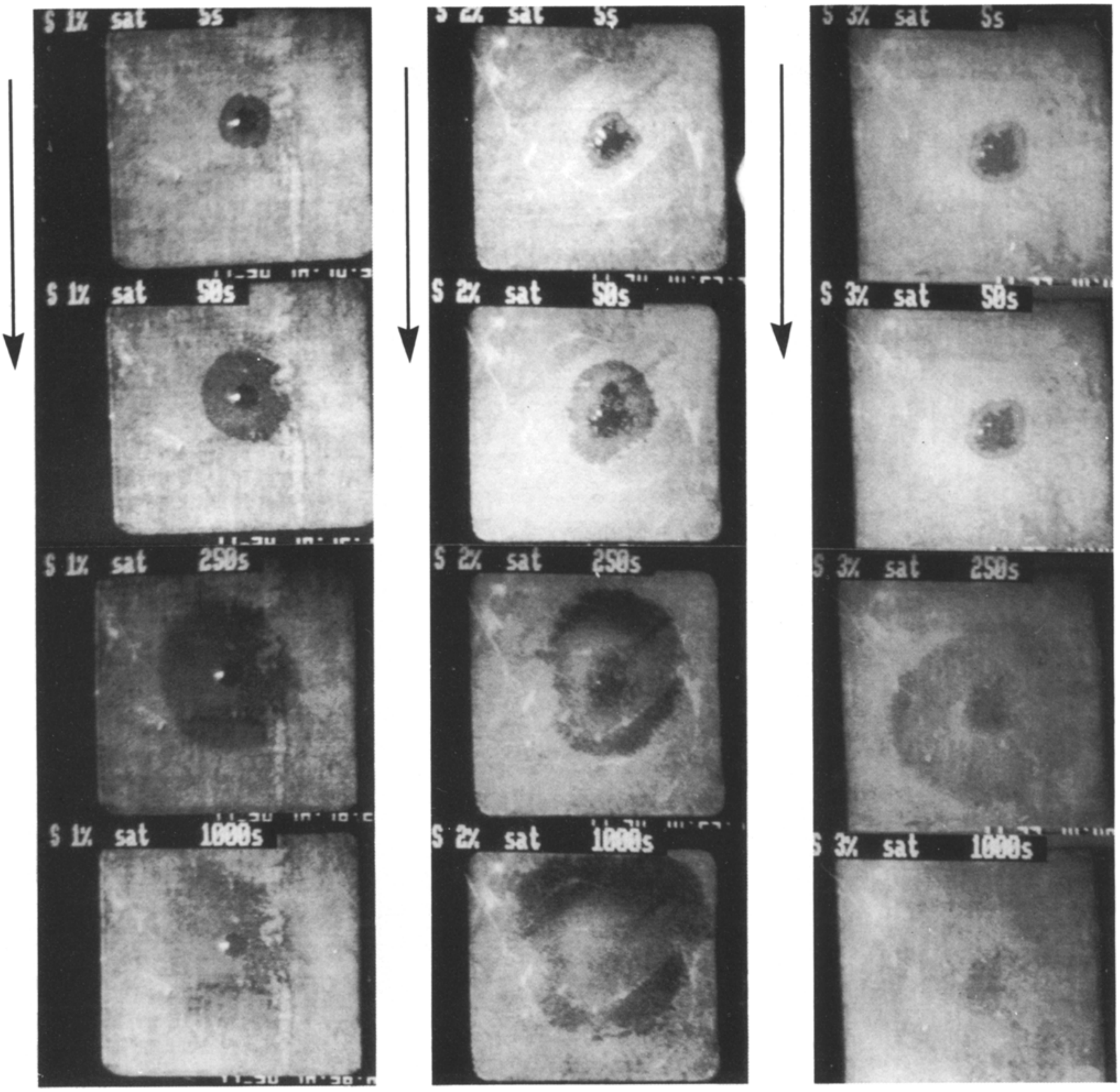

Figure 15 Photographs, at several times, of droplets of S-emulsions spreading on rough steel.

probably zero and the liquid surface tension was always lower than γ_c; γ_c is now quite low, and a small change in surfactant concentration is sufficient to reverse the previous inequality and makes $\gamma > \gamma_c$: it induces retraction of the film and dewetting of the steel plate leaving probably some liquid in the micro-scratches of the plate and eye-invisible droplets.

The spreading of the cap can occur finally because, after retraction, the liquid (mainly water) again finds favourable surface energy.

The rust formation is in complete agreement with the proposed explanation; indeed it developed totally on the surfaces which were never in contact with the droplet but with water vapour, very slightly where

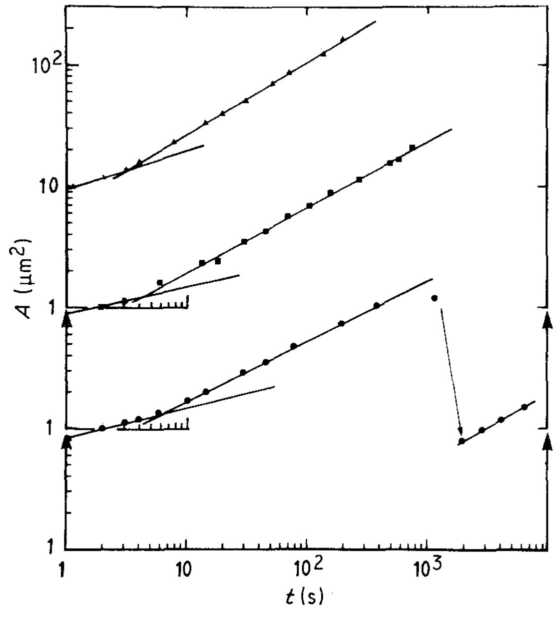

Figure 16 Spreading of S-emulsions: droplet area plotted against time (▲ 3%, slope = 0.31, 0.61, ■ 2%, slope = 0.23, 0.54; ● 1%, slope = 0.24, 0.51).

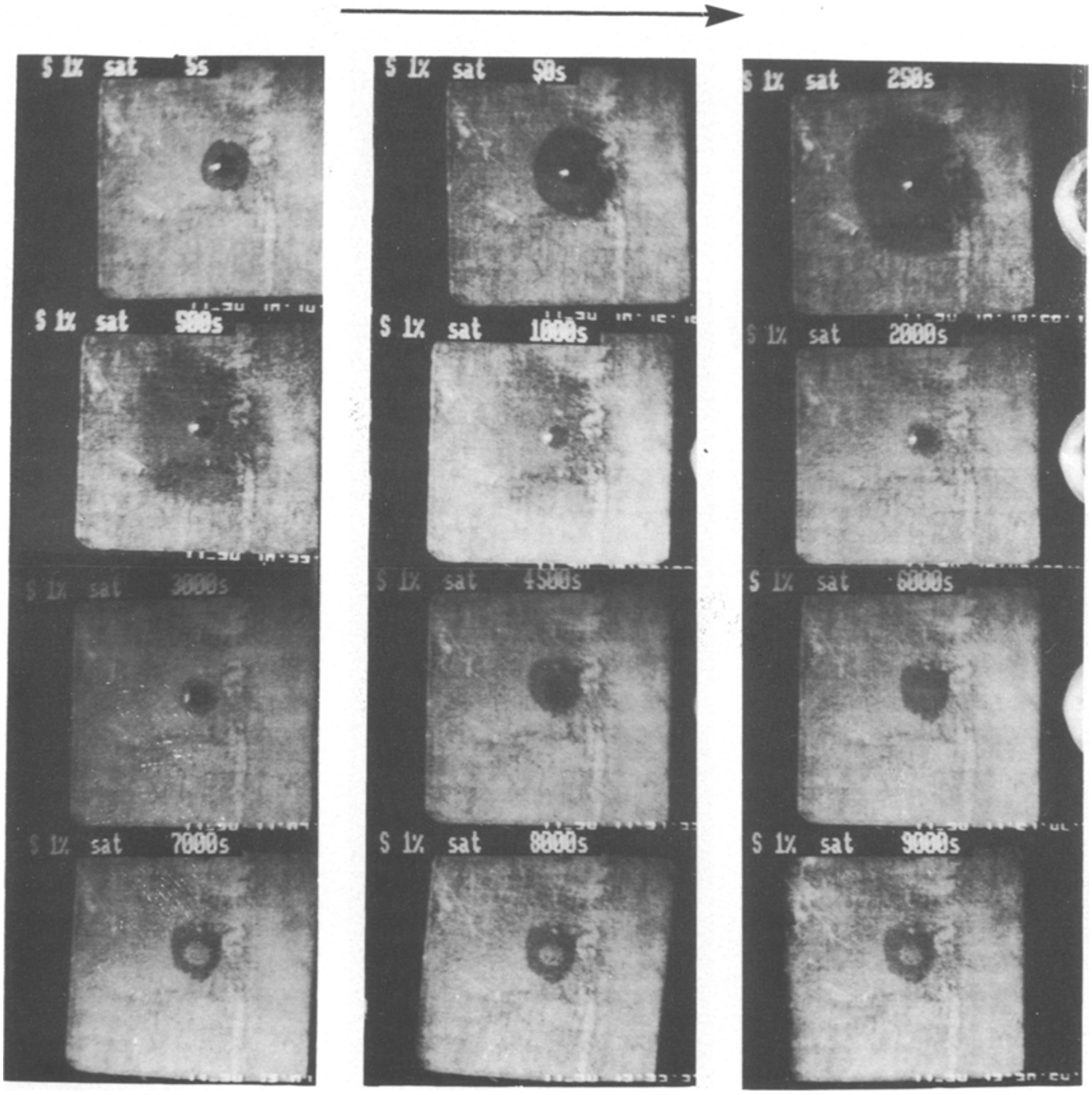

Figure 17 Photographs, at several times, of droplets of 1% S-emulsion spreading on rough steel.

there have been some coverage (in the first step) and there was total protection under the cap.

4.3. Thinning of the central zone

With 1% S-emulsion, at long time (~ 6500 sec), the film (Fig. 7) thins at the location of the central cap and there is formation of a dimple. The reason for this is far from clear. There has obviously been some slow drainage from the central cap towards the droplet periphery which could be due to disjoining pressure variation.

Actually it may have been some diffusion and further adsorption of surfactants at the periphery of the film. The radius of the central thinned spot is about 1 cm which would have been covered in 6500 sec; it gives a diffusion coefficient $\mathscr{D} = kl^2/t \sim 1.5 \times 10^{-4}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$, it is a plausible order of magnitude. In any way such an effect constitutes a real drawback for the plate storage.

5. Conclusion

The very simple test presented in this paper together with the sedimentation test presented in a companion paper [15] should help the choice of an appropriate rolling oil. As already emphasized, oil compositions are essentially unknown. We just know that T-oil rolls very well but makes the plate very "dirty", B-oil is convenient and S-oil was disastrous.

As a matter of fact, the three oils could pass the usual homologation, they behave in a very similar way when they are used pure. The main changes occur when their emulsions are used and their long time behaviour is observed. The T-oil spreads very regularly, forming a thick film which strongly adheres to the plate.

The irregular thickness of the final film of S-emulsion is evidently a strong drawback inasmuch as S-emulsion is totally destabilized in sedimentation tests while it was *a priori* the more stable.

Finally the B-emulsion spreading is nothing but normal.

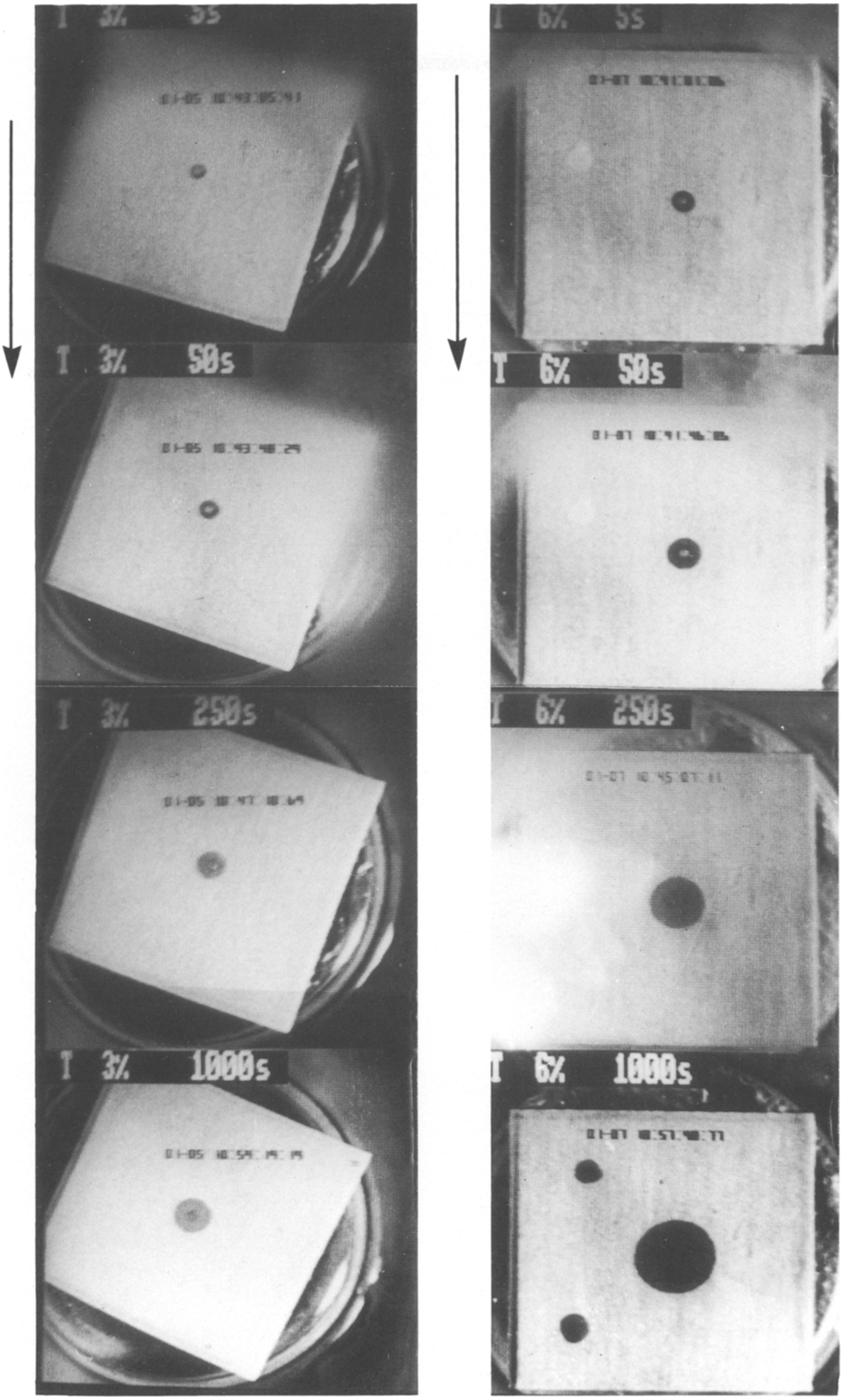

Figure 18 Photographs, at several times, of droplets of 3 and 6% T-emulsion spreading on rough steel.

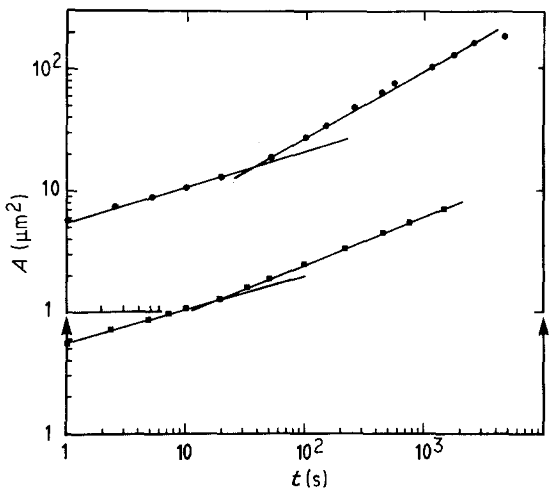

Figure 19 Spreading of T-emulsion: droplet area plotted against time (● 6%, slope = 0.26, 0.57, ■ 3%, slope = 0.27, 0.43).

Acknowledgements

The authors would like to acknowledge the SOLLAC Company for its financial and technical support during this work.

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Received 9 October 1989
and accepted 19 February 1990