

Table 1. RETARDATION OF WATER EVAPORATION BY VARIOUS SYSTEMS

Treatment	Amount of treatment* (g)	% Retardation efficiency † after 13 days outdoor exposure	% Retardation efficiency † after 20 days outdoor exposure
Long-chain fatty alcohol ‡	0.1	59.0	34.4
Oil-surfactant§	0.1	38.5	25.4
Oil-surfactant§	1.0	94.8	82.1
Oil-wax-surfactant§	0.1	79.5	46.3
Oil-wax-surfactant§	1.0	100	98.0

* The area of the surface was 0.835 ft.².

† Retardation efficiency was calculated as:

$$100 \times \frac{\text{Average change in depth of control} - \text{average change in depth of treatment}}{\text{Average change in depth of control}}$$

‡ Archer Daniels Midland's 'Adol 54' (commercial mixture of mainly *n*-hexadecanol and *n*-octadecanol) was used in isopropyl alcohol solution.

§ Applied in a hexane solution.

An oil-wax-surfactant system may have some advantages over a fatty alcohol system. Such systems float more easily, re-form more easily on disturbance, are biologically more inactive, less expensive, etc. However, many important problems remain to be investigated.

I am now investigating the system more closely in an attempt to gain control of the important variables. I am also co-operating with other interested groups in evaluating the practical possibilities of such a system.

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¹ *Retardation of Evaporation by Monolayers*, edit. by La Mer, V. K. (Academic Press, 1962).

² U.S. Dept. Interior Publication: *Water-loss Investigations: Lake Hefner 1958 Evaporation Reduction Investigations* (1959); U.S. Dept. Interior Publication, *Chem. Eng. Rep. No. S1-32: 1960 Evaporation Reduction Studies at Sahuaro Lake, Arizona, and 1959 Monolayer Behavior Studies at Lake Mead, Arizona-Nevada and Sahuaro Lake, Arizona* (1961); U.S. Dept. Interior Publication, *Chem. Eng. Lab. Rep. No. S1-33: Water Loss Investigations Lake Cachuma—1961 Evaporation Reduction Investigations* (1962).

³ Docking, A. R., Heymann, E., Kerley, L. F., and Mortensen, K. N., *Nature*, **146**, 265 (1940). Powell, R. W., *Trans. Faraday Soc.*, **39**, 311 (1943). Nelson, F. C., U.S. Patent 2,170,644 (1939). Heymann, E., and Voffe, A., *Trans. Faraday Soc.*, **38**, 408 (1942). Gilby, A. R., and Heymann, E., *Austral. Sci. Res.*, Ser. A.1, 197 (1948). U.S. Dept. Interior Publication, *Chem. Eng. Lab. Rep. No. S1-12: Reservoir Evaporation Control Screening Tests on Monolayers and Duplex Films* (1957).

⁴ Eckert, F. W., and Hall, K. M. U.S. Patent 3,095,203 (1963).

Solubility of Polyethylene Terephthalate

It is generally considered that polyethylene terephthalate is soluble only in a restricted range of rather specialized organic liquids, such as *o*-chlorophenol, tetrachlorethane/phenol, etc. It is the purpose of this report to describe conditions under which this range may be extended.

In the course of investigations into the mechanism and kinetics of the liquid-induced crystallization of amorphous polymer it has been postulated that crystallization occurs on a progressive front accompanying the diffusion of the particular liquid¹. It was further considered that if this was by a two-stage process involving first of all solubilization and then crystallization it might be possible to isolate the first of the stages by correct choice of experimental conditions. Subsequent experimental verification of this view was obtained with chloroform and *sym*-tetrachlorethane separately using samples of amorphous film (8 × 10⁻³ cm thick) in the two liquids at approximately -40° C. On standing overnight a precipitate formed, which on evacuation of liquid compacted to a hard solid of density 1.42 g/c.c. crystalline when submitted to X-ray diffraction analysis.

Since the polymer is apparently insoluble in these liquids at room temperature, it would suggest that any solubilization which occurs is immediately followed by crystallization. It is interesting to note that in the case of the *sym*-tetrachlorethane at room temperature, splitting of the film takes place. This supports to some

degree a previous contention that in thin films phase separation may arise in the middle of the crystallized material².

That a similar phenomenon of solution and crystallization may be associated with other amorphous but crystallizable polymers is suggested by similar results on isotactic polystyrene³.

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¹ Sheldon, R. P., *Polymer*, **3**, 27 (1962).

² Cottam, L., and Sheldon, R. P., *Nature*, **199**, 202 (1963).

³ Danusso, F., and Moraglio, G., *J. Polymer Sci.*, **24**, 161 (1957).

Temperature Dependence of Contact Angles

THERE are very few recorded observations on the temperature coefficient of contact angles¹. These suggest that the coefficient is very small, if not zero, which is at first sight surprising. Adam² has pointed out that, as a consequence, "it appears that temperature affects the surface tension and the adhesion to the solid to very nearly the same proportionate extent". He has discussed this in terms of the thermal motions of the liquid, and has suggested that "the decrease in the adhesive field of force with rising temperature is much less in solids than in liquids and is due principally or wholly to translatory motion". The implication, however, that the temperature coefficient of the free surface energy of solids is negligible because translatory motions are absent seems to require further justification.

It may be of importance to note that water was present as a liquid phase in all the cases cited by Elliott and Riddiford¹, and by Adam², since Neumann³ has recently reported an appreciable decrease in the contact angles for several organic liquids against their saturated vapours, on a siliconed surface, when the temperature is raised from 12° to 28° C. Zisman⁴ has argued that since the surface tension of a liquid decreases with rising temperature, the contact angle, θ , should also decrease, but, as with Adam's suggestion², this view appears to require the assumption that the temperature coefficient of the free surface energy of the solid is negligible.

The matter is one of both theoretical and practical importance. Consider Young's equation for a liquid against its saturated vapour on a solid surface:

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} - \pi \quad (1)$$

where γ_L , γ_S and γ_{SL} , respectively, are the free surface energies of the liquid, of the film-free solid and of the solid/liquid interface, π being the equilibrium film pressure. It is clear that the theoretical calculation of $d \cos \theta / dT$ would require knowledge of the individual free surface energies and of their temperature coefficients.

Some progress has been made. Fowkes⁵, for example, has shown that internally consistent calculations of interfacial free surface energies can be made on the assumption that the energy of interaction between two phases is purely dispersive. On this valuable line of approach:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^d \cdot \gamma_L^d)^{\frac{1}{2}} \quad (2)$$

where γ_S^d and γ_L^d , respectively, are the dispersive components of γ_S and γ_L (ref. 6) and equations (1) and (2) permit the evaluation of γ_S^d from contact angle measurements for cases in which $\pi = 0$. In certain cases, γ_S^d can also be evaluated when π is finite, and an estimate of