Evaporation of Water: Its Retardation by Monolayers

Spreading a monomolecular film on the surface is a tested and economical means of reducing water loss.

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The ever-increasing growth in population of urban areas and the concomitant increase in the population of the arid areas of all continents requires more rigorous conservation of our most precious natural resource—water. Figures for the projected consumption of water for drinking, for sewage dilution, and for agriculture in the United States indicate that demand will exceed supply by the year 2000. Research in all aspects of conservation and renovation is therefore warranted. The extent of losses by evaporation is, by the very nature of these losses, not easily appreciated by the layman, yet measurements show that from impoundments in the 17 Western states of the United States, 15.6 million acre-feet (19.2×10^9 cubic meters) of water are lost by evaporation alone each year; this loss is equivalent to a disappearance of all the usable water in storage in California, the most populous state in the United States. Control of evaporation, a topic discussed in detail by a recent review panel (*1*), can be accomplished best by decreasing the exposed area of a water storage or by laying a monomolecular film (a monolayer) upon the surface to suppress the rate of evaporation, or by a combination of the two methods.

The idea that a layer of an oily substance will retard evaporation is an old one, dating back to Benjamin Franklin's experiments. However, only within the past decade has it been demonstrated conclusively that a compressed, molecularly oriented monolayer (which is exceedingly thin, and a better retardant that the molecularly disorganized multilayer of an ordinary oil film) will be effective under field conditions. In 1943, Irving Langmuir and Vincent Schaefer (*2*) substantiated Eric Rideal's pioneer finding (1925) that monolayers of long-chain alcohols were effective suppressants of the evaporation of water. Australian workers, in particular William Mansfield (*3*) and R. G. Vines (*4*), after preliminary laboratory experimentation, then developed successful methods for applying such monolayers on the surface of large water reservoirs to control evaporation (*5*).

In 1952 La Mer and his co-workers (*6–11*) continued Langmuir's work in an extensive series of laboratory investigations in which the properties to be sought in a monolayer for evaporation control were investigated in detail. The primary aim of these researches was to gain knowledge of the molecular mechanism involved in the retardation of evaporation, and understanding of the permeability of films in general, by studying the influence of molecular architecture. This was accomplished through study of the rate of evaporation, in terms of the state of compression of the film, and the temperature dependence, by means of the Arrhenius equation. The method of Langmuir and Schaefer (*2*) for measuring the rate of evaporation is satisfactory when properly modified, as in the Columbia University Evaporimeter, for investigating the influence of the molecular architecture of the molecules composing the monolayer. This method gives a quantitative measure of the resistance to evaporation, uncomplicated by motion of the air above the monolayer or by any other of the disturbing influences which had vitiated the results of previous investigators.

However, it has been shown by Archer and La Mer (*6, 7*) that Langmuir's method of spreading the film, by using benzene as a spreading solvent and then compressing to the desired surface pressure, yields results which are difficult to reproduce and which defy simple explanation or interpretation.

The concise term *spreading solvent*, although in common use in the technical literature, has seemed ambiguous to some readers unfamiliar with monolayer techniques. Clarification is needed.

The rate of spreading of solid alcohols is strongly dependent upon the chain length of the molecule, increasing exponentially from a low value for $C_{22}OH$ to a value about 2400 times more for $C_{14}OH$. Benzene and petroleum ether (hexane) have been used for many years as volatile solvents for the less soluble long-chain molecules. These solvents facilitate the rate of spreading. In the case of the long-chain solutes, it is the solvent molecules of the solution which supply the driving force for spreading. They carry the nonspreading solute molecules along, leaving, on evaporation of the solvent, a monolayer of supposedly pure solute molecules.

It had been assumed, until Archer and La Mer (*6, 7*) raised the question in 1954, that the spreading solvent evaporates completely. These workers found that benzene, in contrast to hexane, does not evaporate completely, despite its volatility, but is retained in the monolayer, producing molecular areas (holes) of low resistance to the passage of water vapor; in other words, benzene yields a porous film. This finding has proved to be of great importance not only for the interpretation of resistance measurements made in the laboratory but in the selection of solvents, like kerosene, for field use.

More recent investigations at Columbia University, with monolayers spread from flaked solid hexadecanol dusted on the water surface and with others spread by means of the solvent petroleum ether (hexane), have eliminated this difficulty and have demonstrated (i) the important effects of impurities on monolayer performance, (ii) the lateral pressures needed (*12, 13*), and (iii) the effects of capillary waves (ripples) (*14, 15*) on stability of the monolayer and their role in evaporation phenomena. The research and engineering aspects of evaporation control, as of 1962, are treated in detail in a recent monograph (*11*).

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Principles

General. The transport of a molecule of water from the liquid state, through the monolayer, to the vapor state is a kinetic process involving the surmounting of a number of successive energy barriers: barriers at the water surface; the monolayer; a diffusional barrier as the water is transported through the overlying layer of air which extends to the absorbing substance used as a detector; and barriers at the absorbing interface.

If the effect of the chemical structure of the monolayer is to be measured precisely and meaningfully, these energy barriers, with the exception of the monolayer, must be maintained not only constant but at a minimum value in relation to the sum of all barriers. This is accomplished by absorbing the water which evaporates onto a dessicant contained in a plastic box of known area; the dessicant rests upon a permeable membrane of silk or other fabric. The membrane is supported 1 to not more than 8 millimeters above the monolayer; this reduces to a minimum the layer of air through which the water vapor diffuses and completely eliminates turbulence. Under these conditions the water molecules emerging from the surface of the monolayer diffuse directly to the surface of the dessicant, where they are condensed and weighed.

The individual energy barriers act like a set of resistances in series and are therefore linearly additive. By recording results for the energy barrier in terms of resistances, rather than in terms of rates of conduction (the resistance is the reciprocal of the rate of conduction), the interpretation and particularly the algebra involved are greatly simplified. This scheme of analysis is now becoming a well-recognized procedure for a more simplified treatment of rates of successive reactions in chemical kinetics.

The difference in overall resistance as measured when there is a film (or monolayer) and when there is no film gives the specific resistance due to the film alone, uncomplicated by any other factor. In other words, from such measurements the specific evaporation resistance (r) for the monolayer can be calculated, from the equation

$$r = a\,(W_w - W_d)\,(t/m_f - t/m_w) \quad (1)$$

where a is the area of water surface below the desiccant; W_w and W_d are the equilibrium concentrations of water vapor for water and desiccant, respectively; t/m is the reciprocal for rate of evaporation; and f and w refer to the surface with film and without film, respectively.

The resistance r is a property of the monolayer; it does not depend on any particular form or arrangement of the apparatus. It is expressed in absolute units (in seconds per centimeter).

Molecular architecture of the monolayer. If a monolayer is to retard evaporation, it must have a flexible but condensed structure. The architecture of the molecule—specifically, the length of the hydrocarbon chain, the nature of the polar group, the branching of the chain, and the unsaturation in the chain—determines how molecules will pack together in the monolayer.

Rosano and La Mer (*8*) have shown that straight-chain alcohols and acids, with alkyl chains free of branching and of double bonds, are the materials which form the best condensed monolayers. Most esters, for example, yield monolayers of negligible resistance to evaporation. The alcohols, being more compressible than the esters, yield monolayers more resistant to evaporation in the surface pressure range between 25 dynes per centimeter and collapse. (For the correspondence between surface pressure, dyne/cm, and a three-dimensional pressure, dyne/cm^2, see Adamson, *8a*). In Fig. 1 (top) is shown the effect of alkyl chain length of *n*-paraffinic alcohols on the resistance to evaporation at constant surface pressure and temperature. The increase in resistance (r) to evaporation at a given pressure is related to the chain length (n) of the alcohol by a linear relation between n and log r. This exponential form suggests that transport of water through the monolayer is an activation process (see *6, 7, 16, 17*), involving energy barriers, given by the equation

$$r = A \exp(-nE_{\mathrm{CH_2}}/RT) \quad (2)$$

where A is a pre-exponential factor; $E_{\mathrm{CH_2}}$ is the experimental activation energy per CH_2 group accompanying the process of transport of water through the alkyl portion of the close-packed monolayer; R is the gas constant; and T is the absolute temperature. Equation 2 is more generally expressed as:

$$r = A \exp(-E/RT) \quad (3)$$

where E is the *total* free energy of activation for the transport of a water molecule between bulk water and air; it is made up of contributions due to interactions between head group and water, head group and head group, methylene and methylene, and methylene and water (*16, 17*). (The term *head group* refers to COOH, OH, or any similar terminal group of the monolayer molecule.)

An analysis of resistance to evaporation in terms of Eq. 2 yields values for $E_{\mathrm{CH_2}}$ of 255 ± 10 calories per mole for the alcohols. Recent calculations (*13*) confirm the earlier conclusion of Blank and La Mer (*17*) that this energy corresponds to the energy required for the formation of a hole in a close-packed monolayer against the attractive forces between the alkyl chains.

Chain length is the most important single parameter of the molecular architecture in that it controls not only the resistance to evaporation but also (i) the rate at which material spreads and forms a monolayer, (ii) "squeezing out" of one component of a monolayer by another, (iii) "squeezing out" or rejection of nonvolatile solvent (or solute) impurities spread with the aid of a solvent, (iv) resistance to the action of wave or wind, (v) regeneration or sublimation of the long-chain alcohol in water, and (vi) degradation of the monolayer through the action of bacteria. The action of bacteria has been examined by Chang (*18*), and the evaporation and solution of the alcohol itself have been treated by other workers (*19*). Recently Healy and La Mer (*15*) presented a quantitative analysis of the effects of waves on the monolayer.

The great importance of rate of spreading as a function of chain length is well illustrated in Fig. 2 (*20*). In Fig. 2 are shown the specific resistance to evaporation (*21*) and the initial spreading rate dN/dt (*22*) for a homologous series of long-chain alcohols (dN/dt represents the number of molecules that must spread per second to give a surface pressure of 0.1 dyne/cm).

From the point of view of selecting a suitable material, the relative emphasis to be placed on resistance and spreading rate must be adjusted for any particular field situation; for example, the high resistance of the C_{22} monolayer is associated with a disappointingly low spreading rate. Alcohols with 16 to 18 carbon atoms are found to be most suitable for field application. However, since high temperatures increase spreading rate, the inclusion of

C_{20} and C_{22} components in a commercial mixture of long-chain alcohols for use on warmer bodies of water could be advantageous.

Mixed monolayers. The desirability of using mixtures of compounds with molecules of different chain lengths to attain optimum properties in a monolayer for retarding evaporation has been investigated by Barnes and La Mer (*16*), with alcohol-alcohol and alcohol-acid mixtures. At pressures exceeding 15 dynes per centimeter the alcohol-alcohol monolayers proved to be ideal; they obeyed a mixing law based on the additivity of activation-free energies, G_{12}, of the mixture and G_1, G_2 of the pure components; thus,

$$G_{12} = X_1 G_1 + X_2 G_2 \qquad (4)$$

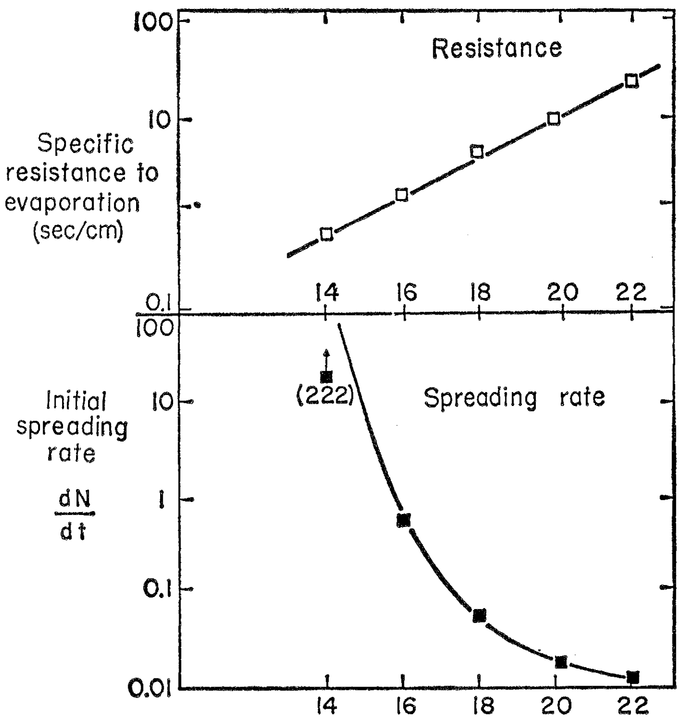
where X_1 and X_2 are the mole fractions of components 1 and 2 of the mixture. Equation 4 expressed in terms of specific resistances becomes:

$$\ln r_{12} = X_1 \ln r_1 + X_2 \ln r_2 \qquad (5)$$

More recent work by La Mer, Aylmore, and Healy (*23*) demonstrated that, for close members of a homologous series, Eq. 5 describes the behavior of mixtures at all pressures, provided materials of high purity are used. Figure 2 illustrates the excellent agreement between theory for ideal surface solutions and experimental results for mixed (1:1) monolayers of long-chain alcohols (*23*). Curves *A*, *B*, and *C* of Fig. 2 are calculated from Eq. 5 and from the values for specific resistance of the pure components. Alcohol-acid mixed monolayers are nonideal and exhibit positive deviations from such ideal behavior, due to the fact that the residual free energy of activation for these alcohol-acid solutions is greater than that for acid-acid or alcohol-alcohol groups (*16*).

Impurities. Most impurities, including the short-chain alcohols, produce a decrease in resistance to evaporation and in surface pressure with time. In the laboratory, the resistance to evaporation can be restored if the barriers are continually compressed to maintain the proper surface pressure. At such pressures (20 to 40 dyne/cm), the short-chain impurities are ejected slowly from the monolayer, forming minute lenses on top that do not affect the porosity. Impurities in a monolayer-forming material cause the curve, in a plot of resistance to evaporation versus surface pressure, at constant temperature, to exhibit a "kink," or point of inflection, at low pressures, as shown in Fig. 2 (curve *D*). By means of successive purifications this kink is removed, giving the smooth isotherm for the purified material (*12*). Note that the melting points of materials given in Fig. 3 are not a sensitive criterion of purity. The variation of resistance to evaporation, with time, for impure materials has been discussed in detail by La Mer and Aylmore (*12*). In specifying materials for practical use, it becomes necessary to distinguish between those impurities which are retained in the monolayer, and which thus decrease resistance to evaporation, and those which are rapidly squeezed out of the monolayer at low pressure. The latter have little effect on the efficiency of the monolayer.

It cannot be emphasized too strongly that it may be a waste of time and money to use materials in the field before adequate tests have been made under controlled laboratory conditions to ascertain their effectiveness. Some



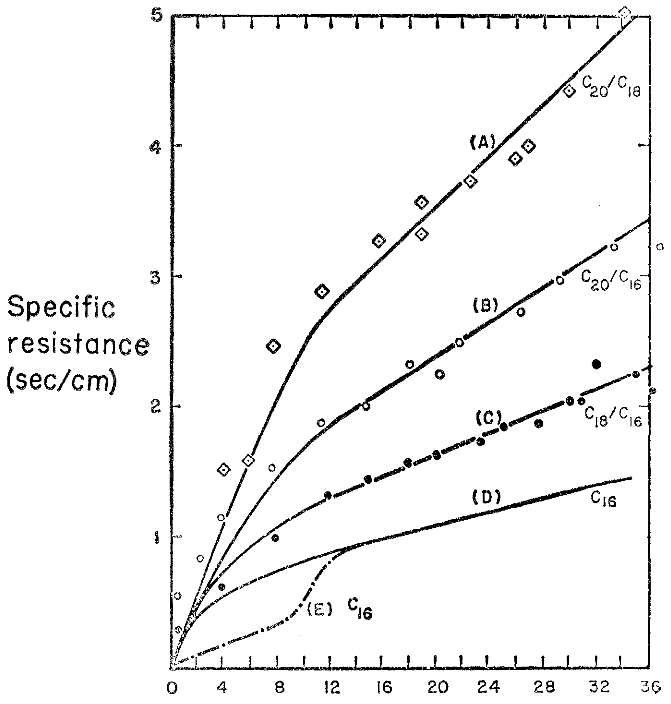


Fig. 1 (left). (Top) Effect of chain length (number of carbon atoms in the chain of the paraffinic alcohol molecule) on resistance to evaporation (*r*, expressed in centimeters per second) [From data of Aylmore (*23*)]. (Bottom) Plot of chain length (abscissa) against initial rate of spreading (ordinate) [Data for rate of spreading from Deo (*22*)]. Fig. 2 (right). Plot of specific resistance against surface pressure, at constant temperature, for mixtures of paraffinic alcohols (from experimental data. (*A* to *C*) Curves for 1:1 mixtures of *n*-alcohols calculated on the basis of the values for free energy in Eq. 5. (*D*) Curve for pure $C_{16}OH$. (*E*) Curve (kinked) for $C_{16}OH$ containing a small amount of impurity, which is squeezed out at pressures above 12 dyne/cm [Based on data of Barnes and La Mer (see *1*)].

of the failures in field tests can be attributed to the use of materials which were later shown to be of poor chemical grade.

Spreading solvents. The effect of the spreading solvent on the resistance to evaporation of a monolayer of hexadecanol or octadecanol is shown in Fig. 4. Use of petroleum ether (*n*-hexane) as a spreading solvent does not reduce the resistance of the hexadecanol monolayer at any pressure. This is evident from the close correlation with resistance of monolayers spread from flaked, solid hexadecanol. The curve for hexadecanol spread by means of benzene is of the same general form as the curve obtained when petroleum ether is the solvent, but at lower pressures the resistance of monolayers spread by means of benzene is considerably less than the resistance of those spread by means of *n*-hexane. This finding is in agreement with Archer's work of 1954 (*6*). At pressures greater than 35 dynes per centimeter the two curves approach each other, and they would meet if pressures as high as 45 to 50 dynes per centimeter could be attained.

These findings confirm the suggestion made by Archer and La Mer (*6, 7*), and later examined in detail by La Mer and Robbins (*24*), that the use of benzene as a spreading solvent lessens resistance of the monolayer to evaporation, since the benzene is retained in the monolayer.

Note that the curve for hexadecanol spread by means of benzene has no "kink" due to "squeezing out" or rejection of the benzene into the water. In this case, the benzene is apparently retained rather than squeezed out.

On the other hand, when we use kerosene as the spreading solvent we find a pronounced "kink" due to "squeezing out" of nonvolatile constituents of the kerosene. The effectiveness of this rejection process is evidenced by the fact that the curves for hexadecanol or octadecanol spread by means of (i) *n*-hexane and (ii) kerosene coincided at pressures greater than 30 dynes per centimeter.

Thermal history of monolayer materials. The rate at which a solid alcohol spreads and forms a monolayer is influenced to a remarkable extent by thermal pretreatment of the sample. Figure 3 represents the kinetics of spreading of two hexadecanol samples (*20*), one formed by rapid quenching from the melt, the other, by slow cooling over several hours. The curve for spreading of hexadecanol mixed with *n*-hexane is included for comparison. The rates of spreading, expressed as molecules per second per dyne, differ by a factor of approximately 5, the slowly cooled sample spreading more rapidly. The x-ray diffraction studies by Benton (*25*) and the Australian workers (*26, 27*) reveal that any one of three processes or conditions—rapid cooling (quenching), the presence of longer-chain alcohols, or cooling in the presence of water—preserves hexadecanol in the α-phase. This phase is metastable and transforms very slowly to the rapidly spreading, sub-α, phase.

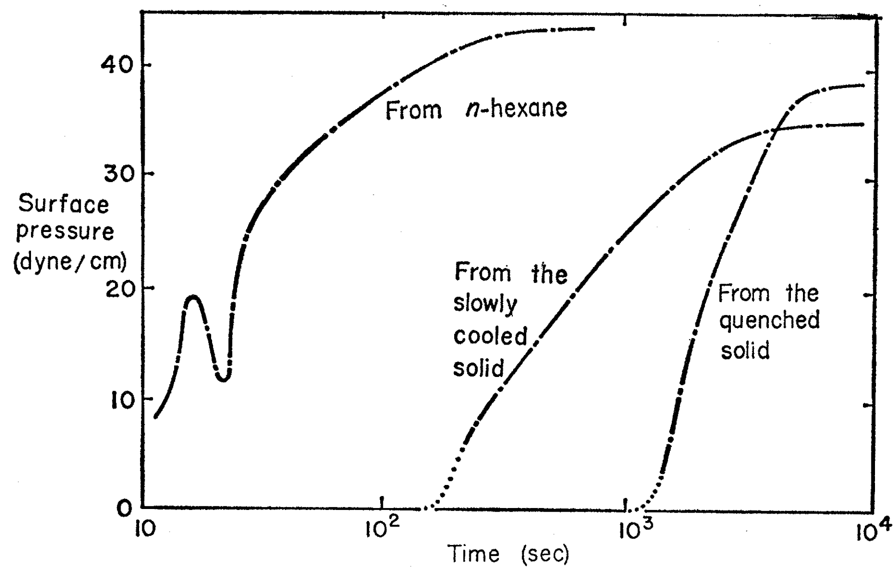


Fig. 3. Curves for rates of spreading (at 25°C) of pure hexadecanol (i) spread by means of *n*-hexane as solvent, (ii) spread from flakes of solid sample formed by slow cooling from the melt (see text), and (iii) spread from flakes of solid sample formed by quenching from the melt. [From La Mer and Healy (*20*)]

This finding highlights the need to preserve hexadecanol in the sub-α form during field operations, to promote rapid spreading. These studies on spreading, carried out with the Columbia University Evaporimeter, all point to the desirability of using well-tempered flakes of solid alcohols as monolayer material.

Capillary waves. Monolayers have long been known to damp out capillary ripples (that is, waves whose velocity is controlled by interfacial rather than gravitational factors) (*28*). Such ripples are known to exist along the profiles of gravity waves (long-wavelength waves) particularly in the "breaking" zone. In damping out these capillary waves, the monolayer absorbs energy from the disturbed surface. At surface pressures below about 15 to 20 dynes per centimeter the ripples only increase the area of the water surface. At higher pressures, and with sufficiently energetic capillary waves, the monolayer apparently becomes submerged (*15*) and there is an accompanying decrease of about 25 to 30 percent in the resistance to evaporation.

Further studies of capillary waves and their effect on the properties of the monolayer are needed. Waves formed mechanically rather than by air currents passing over the surface of the water will yield the least ambiguous results.

Practical Aspects

Field experiments on evaporation are difficult to assess, since meteorological data on water-storage areas are usually incomplete and losses by seepage cannot be estimated reliably. Table 1 summarizes the results of the more significant field studies.

Wind is the natural variable which has the greatest adverse effect on evaporation control efforts. With winds stronger than 24 kilometers per hour (15 mi/hr), evaporation control through the use of a monolayer becomes difficult. Since the monolayer moves as a mass or "slick" at a rate about 1/30 that of the wind when the wind rate is higher than 3 kilometers per hour (*4*), the monolayer must be replenished from the windward side. Recent experiments in which finely flaked material was dispensed from airplanes to form a monolayer in equilibrium with an excess of

Table 1. Summary of some of the more significant field studies. [From a report by V. K. La Mer to the Desalination Research Conference of the National Academy of Sciences (*32*)]

Location	Auspices	Area available (acres)*	Reduction claimed (%)	Reference
Lake Hefner, Okla., 1958	U.S. Bur. Reclamation	2500 (1000 hectares)	9	(*11*, pp. 177 ff.)
Sahuaro Lake, Ariz., 1960	U.S. Bur. Reclamation	1260	23	(*11*, p. 182)†
Lake Cachuma, Calif.	U.S. Bur. Reclamation	3090	22	(*29*)
Nairobi, Africa	F. Grundy	130	60	(*11*, pp. 213 ff.)
Lake Corella, Australia	CSIRO ‡	500	20–50	Mansfield (*11*, pp. 133 ff.)
Umberrumberka Reservoir, Broken Hill, Australia	CSIRO	250	50 §	Vines (*11*, pp. 137 ff.; *33*)
Illinois ponds	W. J. Roberts	Varied	22–43 ‖	(*11*, pp. 193 ff., pp. 198–201)
Eagle Pass, Tex.	R. J. Dressler	50–330	30–63	(*11*, pp. 203 ff.)

* In the tests on the large lakes only partial covering of the indicated area was achieved. † From U.S. Bureau of Reclamation *Engineering Laboratory Report SI-32*; no data on the chemicals used are given in the report. ‡ Commonwealth Scientific and Industrial Research Organization, Australia. § Cost, 2 to 3 cents per 1000 gallons of water saved. ‖ Estimated cost, 8 cents per 1000 gallons saved.

solid particles indicate that this is the most promising method for initial covering of very large water-storage areas; periodic repair of the monolayer from motor boats is then required, under certain wind conditions.

For reasons discussed above, thermal pretreatment of the sample (as in the hot spray technique, which of necessity leads to a rapid quenching of the melt), does not seem to be worthy of further effort.

In laboratory exploration with the surface balance evaporimeter, the difficulty caused by the very slow rate of spreading exhibited by the better retardants of evaporation can be surmounted by dissolving the materials in hexane as the volatile spreading solvent. The areas to be covered in the field are frequently millions of times as large as those to be covered in the laboratory. Hexane is too expensive for field use.

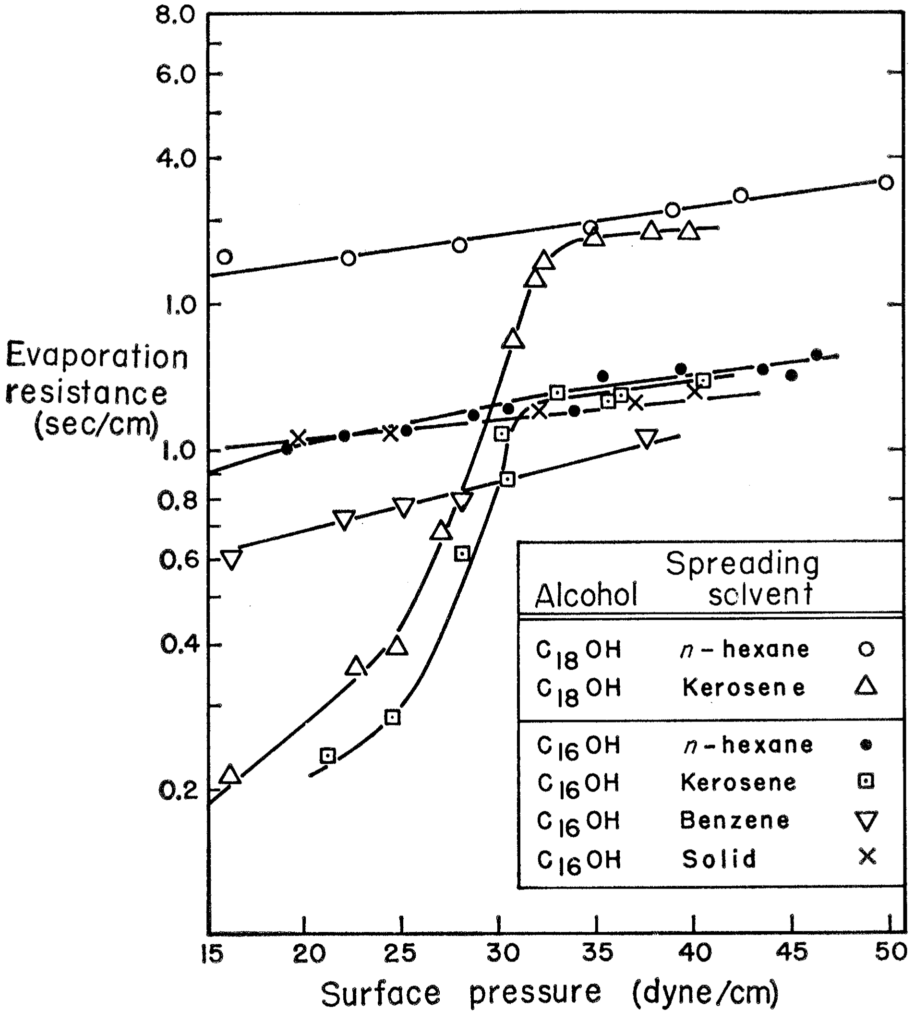


Fig. 4. Effects of three film-spreading solvents on the resistance to water evaporation of monolayers of pure hexadecanol. Curve *X* representing the behavior of monolayers spread from flaked solid hexadecanol is included for comparison. [From La Mer *et al.* (*13*)]

To obtain rapid and adequate coverage, the field tests conducted between 1953 and 1959 were carried out with commercial hexadecanol dissolved in the cheapest solvent available, usually kerosene. The kerosene solution was stored in drums mounted on rafts appropriately located on the lake to take advantage of favorable wind conditions; it dripped from the drums at a regulated rate onto the water surface. Rapid and complete coverage could be achieved, at least for medium-sized storage areas.

The area covered is assessed by airplane observation or from photographs. The photographs are impressive, because the damping of the capillary waves produces high optical reflectance for the areas covered by the monolayer. Unfortunately, good reflectance is not an indicator of effective resistance to evaporation. The monolayers spread from kerosene solutions did not exhibit much resistance. Accordingly, the solvent method has been abandoned.

The engineers in charge of these early operations seem to have been interested only in producing a monolayer covering the reservoir; they paid no heed to research on selection of an appropriate solvent, or to the importance of the chemical composition of the material as indicated by laboratory demonstrations of its effectiveness.

As the common name cetyl alcohol indicates, the only commercial source of hexadecanol has been, until recently, ambergris secreted by the sperm whale. This is an uncertain source of supply, but one sufficient for the limited needs of the cosmetic industry (cetyl alcohol is the principal constituent of lipstick). Later, larger sources of the mixed alcohols were developed as a minor byproduct in soap-boiling processes. The cosmetic industry was quite unprepared, in 1957, to meet the sudden demands for materials for the crash testing programs on evaporation that had just been authorized. Other chemical manufacturers, equipped for large-scale production, betrayed a woeful lack of knowledge and interest in testing to determine the efficiency of their products as retardants of evaporation.

Wealthy ranchers, willing to pay any price for a few pounds of what was referred to as that "magic stuff" to scatter on their ponds, were sold a waxy white powdered solid called hexadecanol. When the levels in the ponds continued to recede, the obvious conclusion was that "the monolayer idea doesn't work." That the "magic stuff" might not be a satisfactory chemical, or that the methods of application were as important as the chemical, were matters that received little consideration.

It is not surprising that hexadecanol fell into disfavor. After the disappointing results of tests on Lake Hefner, Oklahoma, had been published, Barnes and La Mer (*10*, pp. xv, xvi, 36) proved that the material applied in those tests did not meet minimum laboratory standards of performance. The tests that followed were better organized; those on Lake Cachuma in southern California are the latest.

Tests on Lake Cachuma. The commercial hexadecanol-octadecanol mixture (SI-A-40) applied on Lake Cachuma was reported to consist of $C_{18}OH$ (66.2 percent), $C_{16}OH$ (30.4 percent), $C_{14}OH$ (3.3 percent), and $C_{12}OH$ (0.1 percent). The method of analysis was not given; the efficiency was tested by measuring the rates of evaporation from large pans, under stable atmospheric conditions. The data are plotted in Fig. 21 of the *Chemical-Engineering Laboratory Report No. SI-39*, U.S. Bureau of Reclamation (*29*) as the total masses of water evaporated with and without a monolayer. The data are an almost linear function of the time, showing a reduction in the rate of evaporation of 46 to 50 percent when the monolayer was used.

Although a figure of 46 to 50 percent is somewhat lower than that previously recorded for reduction of evaporation in pans when mixtures of $C_{16}OH$ and $C_{18}OH$ were used, one cannot ascribe the lower results to an inferior commercial product, such as was shown to be a principal factor in the disappointing results of the Lake Hefner tests.

In the evaporator pans, breakup of the monolayer by waves produced by the wind is negligible, but, more importantly, the results are not complicated by the very high waves generated by the flotilla of motorboats in this recreation area. The report states (*29*), "boat traffic adversely affected the coverage of the lake . . . [the monolayer] was constantly cut up [particularly] on week-ends. The boat wakes, which destroyed the film, were slow in healing (5 to 60 minutes) and allowed the wind to take advantage of this condition to break up the film."

Other methods of application. Vaughn Hansen and Israelson (*30*) studied coverage on Portola Reservoir by dusting from airplanes. They found that the monolayers produced by successive traverses across the reservoir did not join (or heal) as rapidly when the material was dispersed from a generator producing droplets of a molten mixture of $C_{16}OH$ and $C_{18}OH$ as they did when the material was applied as a dust or flakes obtained by grinding the well-tempered solid. This finding is in complete agreement with the earlier laboratory conclusions of Vines and Meakin (*27*) and confirmed in our more recent experiments (*20*), illustrated in Fig. 3.

By the summer of 1959 the Australians had abandoned both the solvent and the molten spray methods of spreading the monolayer in the field and had turned their attention to developing a simpler apparatus, called the Robertson Grinder-Duster (see *10*, p. 138). A slab of a mixture of $C_{16}OH$ and $C_{18}OH$, about the size of a cake of paraffin for household use, is fed to a rotating steel brush which scrapes the solid material off as fine flakes. These flakes are blown out upon the water by means of a simple agricultural duster powered by a small gasoline motor. The apparatus is mounted in a small motorboat operated by one man, or a larger model is mounted in an airplane. The apparatus is moderately priced, and the labor cost is low.

The objection to the use of powdered material has been that the powder costs more, and, when transported over bumpy roads, fuses and cakes into lumps which are difficult to disperse. The Robertson Grinder-Duster avoids these difficulties and, in addition, the difficulty of melting the material. It was put in operation on Umberrumberka Reservoir (Broken Hill, Australia) in the summer of 1959. One of us (V.K.L.) observed the initial trials, in which this reservoir of 100 hectares (250 acres) was covered with monolayer in 1½ hours; application of the monolayer was followed by a 50-percent reduction in evaporation.

Costs

The costs of evaporation control cannot always be expressed meaningfully in terms of dollar expenditures, since, in certain arid areas, the water saved is so necessary to maintain a productive arable state that the costs are better considered as insurance. Vines (*4*) has reported an expenditure in Australia of only 2 to 5 cents per 1000 gallons (3800 liters) saved. American workers (*31*) find the cost in the U.S. to be between 10 and 12 cents.

It should be recognized that these costs stand out in sharp contrast to the costs estimated for desalination programs, which range from $3 to a speculative $1 per 1000 gallons. Desalination must be encouraged, but the glamor and public appeal of desalination should not be allowed to divert attention and effort from research and development in other areas of water conservation—in particular, from the very thrifty use of monolayers for evaporation control.

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Metabolic Controls in Cultured Mammalian Cells

Cultured cells may provide a direct approach to regulation and function in the whole animal.

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With the widespread experimental use of animal cell cultures, data are accumulating on the factors which control their metabolic activity. Although that information is incomplete and large areas remain essentially unexplored, a summary and assessment may nevertheless be timely. Of particular interest is the relevance of the in vitro findings to metabolic processes in the whole animal. Cultured animal cells may divide every 16 to 30 hours, while the generation time in the whole animal is more often on the order of 30 to 90 days. What is the growth controlling mechanism from which the cultured cell has escaped almost wholly, and from which the cancer cell in vivo has escaped in small part? Can the study of metabolic controls in discrete cultured cells in fact be expected to throw light on their growth in the whole animal, to say nothing of even more complicated phenomena such as differentiation and morphogenesis, senescence, and the malignant transformation? Such processes involve cells of diverse types complexly organized into tissues, in which intercellular effects and spatial orientations difficult to reproduce in culture play an important and perhaps decisive role.

The specific aspects of metabolic controls in cultured cells here discussed have been selected, not because of a single unifying theme, but simply because of their relevance to the work interests of this laboratory. The topics include (i) the possibility that the provision of nutrilites may limit or control growth in vivo; (ii) some of the factors which control or modify the specific enzymatic activities of cultured cells; (iii) the profound effects of cellular interaction on their metabolic activities, with particular reference to population density and contact; (iv) genetically determined variations in metabolic activity, including inborn errors of metabolism, "variant" cells, and the effects of chromosomal aberrations; (v) the metabolic effects of viral infection; and (vi) some of the factors which control the expression of specialized organ function in cultured normal cells. In each case, the mass of published data precludes a complete bibliographic citation (*1*).

Nutritional Controls

The simplest method of controlling the growth and metabolism of cultured cells is to limit the supply of some essential nutrilite. Only 28 growth factors have been shown to be required for the sustained growth of mammalian cells in vitro (*2*), and through control of the input of one or more of these, the average generation time can be varied from 16 hours to 7 days (*3*). Thus, if the intracellular pool of a single amino acid falls below a critical concentration of 0.01 to 0.04 m*M*, there is no demonstrable protein synthesis or cellular growth, and a slight increase in pool size then has an altogether disproportionate effect on the rate of cellular proliferation (*4*). We do not know which of the sequential steps involved in protein synthesis is the growth-limiting reaction controlled by the size of the cellular amino acid pool.

It is, however, unlikely that the local provision of amino acids, glucose, or vitamins limits and controls the rate of cellular growth in a living animal on an adequate diet. Most of these growth factors are present in the body fluids in concentrations far exceeding those required for maximum growth in vitro, and there has been no evidence that cells in tissues differ from cultured cells in their ability to transport and concentrate amino acids, for example (*5*). There is, however, one unknown in the nutrition of animal cells which may conceivably be growth-limiting in the whole animal. Almost all cultured cells require one or more substances deriving from serum protein for survival and growth. (The fact that a small number of cell lines can dispense with the protein-derived factor, or factors, as the result of either adaptation or selection does not affect the general statement.) The active component is apparently not the protein as such, but a relatively small molecule, either a polypeptide or a substance bound to the protein and released from it (*6, 7*), the provision of which may be growth-limiting in vivo. It seems more likely, however, that cellular growth in the whole animal is controlled, not by the supply of an essential nutrilite, but by as yet unknown factors which actively limit or stimulate cellular growth and division. Although growth-inhibitory factors may develop in cell cultures (*3*), and although growth-inhibitory effects are sometimes observed when different cells are grown parabiotically, we know nothing about the nature of the compounds involved, the mechanism of their action, or their relevance to growth control in vivo.

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