

Review of Literature on Evaporation Suppression

By GEORGE B. MAGIN, JR., *and* LOIS E. RANDALL

S T U D I E S O F E V A P O R A T I O N

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STUDIES OF EVAPORATION

REVIEW OF LITERATURE ON EVAPORATION SUPPRESSION

By GEORGE B. MAGIN, JR., and LOIS E. RANDALL

ABSTRACT

Evaporation suppression is the reduction of evaporation by controlling the rate at which water vapor escapes from water surfaces. The need for water saving is greatest in areas of little rainfall and low runoff. Water losses by evaporation from storage reservoirs must be minimized for greatest utility of limited supplies.

A review of the literature shows that evaporation can be retarded by either physical or chemical means. It can be controlled by enclosure in a building, application of plastic covers, oil films, and monomolecular films.

Monomolecular films hold the greatest promise for use on large areas of water such as reservoirs. From the literature available it is apparent that these films introduce many chemical and physical problems. The suppressants must be nontoxic and odorless, especially if used on water-supply reservoirs. They should allow the free exchange of oxygen so that aquatic life is not endangered. The effects of water-borne bacteria on these films and the effects of the films on water of different qualities are not fully known. The physical problem of detecting the presence of the film has not yet been solved. Of the monomolecular films that have been investigated, the waxy alcohols such as hexadecanol and octadecanol show the greatest promise.

INTRODUCTION

Maximum use of a short water supply can be obtained by applying conservation methods, such as storing water at times of surplus for use in times of drought. Unfortunately, not all the water put in surface storage is available for future use because part is lost through evaporation. The evaporation loss is serious because it is usually greatest in dry areas where the supply is most valuable. For example, in the Great Basin and the Colorado River basin, where the needs for water exceed the amounts available, evaporation dissipates almost one-sixth of the available supply (108).¹ Great economic gain would result in all arid areas if as much as one-fourth of the evaporation from stored water could be prevented.

This paper is a brief review of the more significant studies on the theory and methods of reducing evaporation. The work is part of the studies on evaporation

suppression by the U.S. Geological Survey. An extensive search of the literature relating to methods of evaporation suppression discloses significant progress to date and suggests that more effective methods may be developed.

The authors found very helpful the extensive bibliographies of the Southwest Research Institute and of the other writers whose names are preceded by asterisks in the bibliography. However, some of the references in those bibliographies were not used as they did not seem pertinent to the subject matter covered here.

THEORY OF EVAPORATION

Four main factors affect evaporation: the area of exposed water surface—the larger the area, the greater the loss; the temperature of the water and air above it—a higher temperature increases loss; the movement of air above the water surface—a greater movement carries off more vapor; and the relative humidity—dry air absorbs moisture more readily than moist air.

According to the kinetic theory of evaporation, molecules of water are in a constant state of random motion, colliding with one another, and rebounding. In the liquid state, these molecules are held in balance by their cohesive force; however, some molecules possess sufficient kinetic energy to overcome this cohesive force and break free from the water surface, thus forming gaseous molecules.

The fundamental law of evaporation is credited to Dalton (87). His generalized formula of evaporation (88),

$$E = C(P_w - P_a),$$

was proposed in 1834. In his formula

E = rate of evaporation in inches per day;

P_w = vapor pressure in the film of air next to the water surface;

P_a = vapor pressure in the air above the film;

C = coefficient that is dependent upon barometric pressure, wind velocity, and other variables.

¹ Numbers in parentheses refer to references in the bibliography.

Many investigators since Dalton have contributed to the theory and laws of evaporation (see 33, 37, 49, 84, 86, 89, 120, 124, 154, 180, 188, 190, 207, 227, 236, 281, 282). Using theoretical considerations and measured rates of evaporation of water from plane, cylindrical, and spherical surfaces in an air stream, Missenard (212) concluded that evaporation and convection are related and are expressed by the same quantitative laws.

STUDIES OF FACTORS AFFECTING EVAPORATION

Evaporation depends on several factors in addition to the four previously mentioned. Some investigators have considered the effect of barometric pressure and solar radiation. Dalton's (87) fundamental derivation considered the effect of vapor pressures, wind velocity, and barometric pressure. The effect of vapor-pressure differences at the air-water interface has been studied by Matsak (208) and others (36, 39, 120, 159, 207, 229, 312). Tzentnershver (304) investigated the effect of wind velocity and found that the rate of evaporation of water is proportional to the velocity of the air current at the water surface, provided that the temperature in the surface layer of the liquid is constant. Timofeev (294) studied the effects of turbulent air flow. Folse (115) concluded that wind velocities less than 10.8 miles per hour had no effect on evaporation, but that evaporation-pan studies do not seem to support this conclusion.

Stelling (275), in his pan experiments in Russia (1875-1882) worked out an approximate formula based on wind velocity,

$$E = (0.8424 + 0.01056W) (e_s - e_a)$$

in metric units, in which E (evaporation) and the difference in vapor pressure ($e_s - e_a$) are given in millimeters and the wind velocity W is in meters per second. Powell (233), Lur'e and Mikhailov (187), Himus (151), and Carrier and Lindsay (71) studied the effects of wind velocity and temperature. Himus and Hinchley (152) studied the effect of air movement on the rate of evaporation of water below the boiling point. Their paper cites several references. Many other men have studied the effect of wind velocity (31, 32, 76, 85, 98, 117, 120, 153, 190, 208, 209, 213, 225, 227, 229, 280, 281, 282, and 312), but to discuss their contributions is beyond the scope of this report.

Sharpley and Boelter (266) developed an evaporation formula based on the humidity and temperature of the water. From water-surface temperature measurements, Alty (37, 38) calculated the maximum rate of evaporation. Carrier and Lindsay (71, 72) studied the effect of water and air temperature on evaporation. Cummings and Richardson (86) applied a correction factor for temperature to their thermodynamic equa-

tion of evaporation. Others (120, 151, 152, 237, and 238) have used temperature data in their formulas.

The effect of barometric pressure has been studied by Folse (115), Russell (255), and Matsak (208). Quilez (238) criticized the existing formulas for calculating evaporation from a free surface. He derived an expression that does not involve empirical constants and requires the measurements of only air and water temperature and pressure. Other investigators have studied the effects of humidity (85, 86, 207, 266), solar radiation (85), altitude (62), surface area (76, 109, 114, 223, 229, 305), and other factors (148, 149, 154, 306).

Chakravorty (76) studied the evaporation from a free surface that was of restricted area and in which shape, orientation, and edge effect influenced appreciably the overall evaporation.

MEASUREMENT OF EVAPORATION

Evaporation has been determined by several methods. Wisler and Brater (319) list five general methods: The storage equation, measurements in an auxiliary pan and reducing the pan evaporation to natural water surfaces by means of a coefficient, the evaporation formula, the humidity and wind velocity gradient, and the measurement of insolation.

Other men have taken into account many related factors and have proposed different evaporation equations. Fitzgerald (112) modified Dalton's equation by taking into account wind velocity,

$$E = (0.40 + 0.199W) (e_s - e_a),$$

in which W = wind velocity. Carpenter (70) experimented with a sunken tank in 1887. His equation,

$$E = (0.39 + 0.187W) (e_s - e_a),$$

is a modification of Fitzgerald's and is applicable to conditions in western United States.

Boelter and others (61) worked out curves and equations of evaporation at air temperatures between 65° and 80°F. and relative humidity between 54 and 98 percent. They list 13 references. Hickox (150) experimented in still air under controlled conditions. He drew an analogy between heat transfer and mass transfer as they occur in evaporation and expressed evaporation rates in terms of appropriate dimensionless groups. He considered the effect of vapor-pressure differences, wind velocity, pan diameter, water temperature, air pressure, rim height, color of pan, and depth of pan. His report contains 42 references on evaporation, most of which are included in this paper. Others have contributed to our knowledge of measurable factors influencing evaporation (see 76, 114, 115, 151, 180, 184, 187, 255, 266, 275, 306).

Thomas and Ferguson (288) reviewed part of the literature and pointed out the confusion in terms and the variation in formulas developed by different authors under different conditions. Livingston (183) published an annotated bibliography of evaporation.

EVAPORATION SUPPRESSION

The study of evaporation suppression on large areas such as lakes and reservoirs requires a method of evaluating the evaporation that would have occurred during the same period without the suppressant. Comparison of evaporation from two identical reservoirs side by side and similarly oriented is one solution; however, such reservoirs rarely exist in nature. A more commonly used method is a comparison with nearby evaporation pans having concurrent records.

Kohler and others (165, 166) have calculated evaporation from lakes by converting measured evaporation from pans to lake evaporation by applying coefficients. Kohler and others (166) describe a combination mass-transfer and energy-budget approach first suggested by Penman (230).

Blaney (57, 58) studied the effects of high altitudes on evaporation from pans. He adjusted these data to natural lakes and reservoirs by applying a coefficient. The study was inconclusive because the pans froze during the winter.

Sleight (272) used coefficients to convert pan evaporation to reservoir evaporation. Bonython (62), using data from South Australia, demonstrated how errors can be introduced into the use of a tank evaporimeter to derive evaporation rates from large bodies of water.

Blaney (58) compiled data on evaporation from water surfaces in California, and Bloodgood (60) compiled all known data on water evaporation in Texas. Bloodgood also discussed procedures and coefficients to use in adjusting pan evaporation losses to natural lake or reservoir losses.

Bigelow (55) showed that the location of pans relative to the water of a reservoir has an important effect on the calculated evaporation. He concluded that water is evaporated from a lake or reservoir about five-eighths as fast as from an isolated pan placed outside the vapor blanket. Rohwer (250, 252) found that the evaporation coefficient differs for different types of pans and summarized the available records of comparative rates of evaporation from different types of pans and large bodies of water under similar conditions. He discusses the factors that cause evaporation and the derivation of the general law under which these factors operate.

Mansfield (191, 192) used a sunken pan to assess the effectiveness of evaporation suppressants. This

evaporimeter was calibrated to measure evaporation from small ponds that were used in a field test of hexadecanol. Kohler (165) showed that, for a sunken pan used in the Lake Hefner study, the monthly coefficient used to convert pan evaporation to lake evaporation ranged from about 0.2 to 1.5. He concluded that Mansfield's evaporimeter may be satisfactory for measuring evaporation from small ponds but may be subject to considerable error if used for large reservoirs.

Harbeck and Koberg (134) conclude that a better method of assessing the suppression of evaporation may be obtained by using a combination of the energy-budget and mass-transfer evaporation measurement techniques.

The energy-budget method of measurement was suggested by Angstrom (44) in 1920. It is based on the conservation of heat energy within a body. For any given body of water a balance must exist between heat gains and losses. Heat may be gained by long- and short-wave radiation, conduction, and condensation. Heat losses result from direct and reflected radiation, conduction, advection, and evaporation. Radiation, conduction, advection, and changes in energy storage in the water may be measured, and the evaporation or condensation may be computed.

Bowen (64) determined that the ratio of heat losses by conduction and by evaporation from any water surface is

$$R = 0.46 \frac{(T_w - T_a) P}{(P_w - P_a) 760}$$

where R is the Bowen ratio, and T_a and P_a are the original temperature and vapor pressure of the air passing over the lake, and T_w and P_w are the corresponding quantities for the layer of air in contact with the water surface.

Cummings and Richardson (86) use the Bowen ratio in their equation,

$$E = \frac{(H - S - C)}{L(1 + R)}$$

which takes into consideration the net radiant energy absorbed and the heat stored in the water. In their equation, E is the evaporation, H the difference between the incoming and outgoing radiation, S the heat stored in a column of water having unit cross section, C a correction for heat carried by flowing water and leakage of heat through the walls of the vessel, L the latent heat of water, and R the Bowen ratio.

UNESCO (306) published an equation of the thermal balance at the evaporating surface as

$$R = LE + H + G$$

where R =net radiative flux at evaporating surface,
 L =latent heat of evaporation of water,
 E =rate of evaporation per unit area,
 H =rate of transfer of sensible heat per unit area,
 and
 G =rate of change of heat storage per unit area
 below evaporating surface.

"Thus, $R - G = LE + H$ and, if R and G can be measured or estimated, the determination of E and H becomes a matter of correctly assigning the relative magnitudes of these quantities."

Other investigators have worked on the energy-budget approach to evaporation measurement (see 41, 62, 85, 130, 162, 206, 222, 223, 227, 229, 230, 235, 283, 285, 289, 290). E. R. Anderson (41) demonstrated that the evaporation computed using the energy-budget equation was in good agreement with evaporation determined from the water-budget control at Lake Hefner. Harbeck (130, 133) and Harbeck and Koberg (134) rearranged Anderson's energy-budget equation,

$$[Q_s - Q_r + Q_a - Q_{ar} + Q_v] - [Q_{bs} + Q_e + Q_h + Q_w] = Q_s$$

to determine evaporation. Their equation is simply, inflow—outflow=change in storage, in which

Q_s =solar radiation incident to the water surface,

Q_r =reflected solar radiation,

Q_a =incoming long-wave radiation from the atmosphere,

Q_{ar} =reflected long-wave radiation,

Q_v =net energy advected into the body of water,

Q_{bs} =long-wave radiation emitted by the body of water,

Q_e =energy utilized by evaporation,

Q_h =energy conducted from the body of water as sensible heat,

Q_w =energy advected by the evaporated water,

Q_s =increase in energy stored in the body of water.

Some factors, such as heating due to chemical and biological processes, conduction of heat through the lake bottom, and transformation of kinetic energy into thermal energy are small and were neglected.

TECHNIQUES IN EVAPORATION SUPPRESSION

Where water is at a premium, as in the arid regions, man has resorted to various methods of conserving it. Freese (118), in his paper before the First International Conference on Reservoir Evaporation Control, discussed a number of methods of reducing evaporation. Most methods consist of reducing the liquid surface exposed to the atmosphere, and they can be divided into three classes—those that reduce the surface area, those that mechanically cover the surface, and those that cover the surface with a film.

The surface area can be reduced by constructing reservoirs with maximum depth for a given volume (52, 108, 118), storing water underground (52, 108, 118), and storing water in one large reservoir instead of several small ones (52, 118). Evaporation losses may be reduced also by proper selection of reservoir sites (47, 100, 108).

Mechanical covers include roofs (52, 113), floating rafts (52), and wind breakers (52). Fleming (113) describes an aluminum-covered municipal reservoir at Santa Ana, Calif. Although ground-water reservoirs generally do not have exposed surfaces, in many of them large quantities of water are used by phreatophytes—plants that obtain water from the zone of saturation. Therefore, large quantities of water can be saved by elimination of phreatophytes (see 47, 52, 108, 113, 249).

Surface films, the third general classification, appear to be the most economical and offer the greatest potential for evaporation reduction.

Harbeck and Koberg (134) in their studies state:

Application of a film affects the terms Q_{bs} , Q_e , and Q_h , but the net sum of the effects must be zero, or

$$(Q'_{bs} - Q_{bs}) + (Q'_e - Q_e) + (Q'_h - Q_h) = 0$$

in which the symbols with prime refer to the reservoir with a film and the symbols without prime to the same reservoir without a film. If evaporation is decreased, the water-surface temperature must rise until the energy no longer being utilized for evaporation is returned to the atmosphere by increased back radiation and conduction.

Harbeck and Koberg's method (134) of evaluating the effectiveness of a monomolecular film involves the computation of two unknowns—the evaporation and water-surface temperatures that would have been observed if no film had been applied. Two simultaneous equations are used to solve for the two unknowns, one based upon the energy-budget concept and the other upon the mass-transfer theory.

The formation of monomolecular surface films of spreading oils was discovered by Agnes Pockels (232) in 1891. She found that the area covered by a spreading oil, such as oleic acid, could be varied at will by confining the film between movable barriers placed across a shallow tray filled with water. Lord Rayleigh (241) in 1899 reviewed Miss Pockels' work and came to the conclusion that the oil spreads to form a film one molecule in thickness. During the period 1903–13, Henri Devaux (95) studied the effect of oil film on water and the limit of its expansion. He concluded that, if Miss Pockels had scattered an inert powder on the surface to render the film visible, she would have seen the extent to which the oil would spread. He found that the thickness of an oil film at the maximum extension is

only a single layer of molecules and that the film will disappear abruptly when one tries to stretch it thinner.

Marcelin (197-205) studied the properties of benzyl benzoate and oleic acid and their effects on water in terms of the law of Gay-Lussac. He found that the product of the area occupied by a quantity of oleic acid on the surface of water and the surface pressure of the film is constant over the range extending from the saturated surface to that represented by a surface 28 times as large.

Du Nouy (105), in his 1944 article "Concerning the rate of evaporation of water through oriented monolayers on water," referred to his earlier (1924) work (104) as follows:

I should also like to mention the fact that, to my knowledge, I published the first paper on the influence, on the rate of evaporation of water, of a monolayer of oriented molecules. This paper undoubtedly escaped the attention of Dr. Langmuir, as it was printed in the *Journal of Experimental Medicine* under the misleading title . . . I reported a definite slowing up of the rate of evaporation, but my method was crude in comparison with that employed by Drs. Langmuir and Schaefer.

Hedestrand (141) concluded that a monomolecular film of fatty acid reduced the rate of evaporation of water very little, if at all; however, Rideal (243) and Langmuir and Langmuir (176) found that fatty acids spread on the water surface reduce evaporation greatly. Rideal (244-246), Cary and Rideal (73-75), and Schofield and Rideal (258, 259) studied the effects of temperature and polar groups on the equilibrium pressure, investigated the mechanism and rate of spreading, and calculated the latent heat of fusion for some of the organic compounds by an application of the Calpeyron equation.

Langmuir (174) found that a small amount of oil on the surface of water has no appreciable effect on its surface tension, but when the amount of oil per unit area is increased beyond a certain limit, the surface film decreases. From this he concluded that the amount of oil necessary to affect the surface tension corresponds to a layer one molecule thick. He further reasoned that, since the oil spreads on the water and since the presence of $-\text{COOH}$, $-\text{CO}-$, or $-\text{OH}$ groups in an organic molecule tends to render a substance soluble in water, these groups must have a strong affinity for water. This means that the molecules are standing on end with the functional group being dissolved in the water and the hydrocarbon chain extending upwards from the surface. He found that pure hydrocarbon oils (without the functional groups) do not spread on water but form lenses. Langmuir worked out a method for measuring the area occupied by a molecule on the water surface.

Langmuir and Langmuir (176), in their paper "The

effect of monomolecular films on the evaporation of ether solutions," pointed out that, using Rideal's measurements, the resistance to evaporation of water by a monomolecular film of oleic acid is 800 units at 25°C . whereas, in the absence of a film, it is 3 units. Instead of considering the rate of evaporation of a liquid in grams per square centimeter per second, they used the reciprocal of this quantity, termed the evaporation resistance, R , in square-centimeter-seconds per gram. They found cetyl alcohol had a resistance of 65,000 units to the evaporation of water and that the effect can be observed in experiments at 1 atmosphere pressure.

The resistance of cetyl alcohol film ranges from 5,000 units with no wind to 1,900 units with a wind velocity of 1.5 meters per second. The thickness of the film through which diffusion must occur can be calculated by the equation $R=h/CD$, where h is the thickness of a film, D is the diffusion coefficient, and C the concentration of the diffusing substance when equilibrium is brought about by stopping diffusion, $C=10^{-8}$ grams per cubic centimeter for the concentration of water in the cetyl alcohol film.

Langmuir and others (175, 178) studied the effect of oil lenses on water and the nature of monomolecular expanded films. Langmuir and Schaefer (177), in their paper on "Rates of evaporation of water through compressed monolayers on water," pointed out that the rate of escape of water molecules from the surface decreased at the ratio of about 10,000 to 1 in the presence of a cetyl alcohol monolayer. They decided that this evaporation resistance is due to an energy barrier—oil layers reduce evaporation by a different mechanism.

Adam (2) studied the properties and molecular structure of thin films of palmitic acid on water. His views confirmed those of Langmuir that the film consists of a single layer of molecules oriented with their COOH group towards the water. He concluded that the hydrocarbon molecules sink to different depths whereas the molecules with the COOH groups rise in the water, so that the COOH groups are in contact with each other; this arrangement gives a liquid film, whereas the packed hydrocarbon chain normally gives a solid one.

Adam (3-29) studied the properties and molecular structure of thin films for several compounds. His book (16), especially chapter 2, is a good source of information on surface films.

Glazov (122, 123) found that the evaporation of water from flat dishes in an air current is reduced by surface films as follows: cetyl alcohol $> \text{C}_8\text{H}_{17}\cdot\text{OH} > \text{C}_{15}\text{H}_{31}\cdot\text{COOH}$ and $\text{C}_{25}\text{H}_{51}\cdot\text{COOH}$ and $\text{C}_{25}\text{H}_{51}\cdot\text{COOH} > \text{saponin}$. He decided that only liquid films are effective and that the monomolecular layers reduce convection under the surface.

Oil has been used as a retardant for evaporation for many years. Abbe (1) reports on the work of Onofrio, who used oil upon inland rivers and lakes in France to retard evaporation and thereby reduce the formation of fog. Burgess (69) studied surface-film oil to find a stable film with the highest spreading pressure. Cary and Rideal (74) studied the behavior of crystals and lenses of fats on the surface of water and the effect of temperature on the presence of a film in equilibrium.

Gilby and Heymann (121) studied the rate of evaporation of water through duplex films. In the presence of an oil film, wind speeds as much as 8 miles per hour did not increase the rate of evaporation. Guttenberg (127) found that the rate of spreading of oil in water could be expressed by $R=ct^k$ where t is temperature in $^{\circ}\text{C}$., c ranges from 9 to 19 centimeters per second, and k ranges from 0.63 to 0.72 centimeters per second for oleic, linoleic, and linolenic acids. No temperature effect was observed between 10° and 40°C . Hedestrand (141) concluded that the rate of evaporation of water does not depend on resistance to the diffusion of water molecules through the oil film but on the resistance of the stagnant layer of air above the liquid.

Heymann and Yoffe (145, 146) studied "the stability of multimolecular films of hydrocarbon oils, containing spreaders, on water surfaces" and found that polymerized spreaders form thick films of oil that are much more stable than other spreaders; some last as long as 18 months if they are kept free from dust. Langmuir and Langmuir (176) showed that oils have greater resistance to evaporation than other monomolecular layers. Rohwer (251) showed that surface oil films reduce evaporation of water in proportion to their thickness, but the relatively rapid dissipation of oil by wind, rain, or other agents, renders this method uneconomical for the conservation of large areas of water. Nelson (221) has a patent for the use of oil on water to prevent evaporation. Others have studied the effects of using oil to prevent evaporation (see 95, 175, 218, 233, 239, 244, 295, and 296).

The use of multimolecular layers for suppression of evaporation has been studied by Bikerman (56), Langmuir (178), and others (203, 217, 233). The multimolecular films differ from the monomolecular films only in thickness and their properties are very similar. The remainder of this paper, therefore, will be concerned with monomolecular films.

Monomolecular layers are potentially the best evaporation suppressants (77, 79, 80, 155, 243). Intensive study has been made of their chemical properties (see 43, 65, 90, 94, 181, 185, 220, 231, 260, 267, 273, 274, 278, 300, 303). Sebba and Briscoe (263) found that a freshly formed film of *n*-docosanol under a surface pressure of 47 dynes per centimeter almost completely prevents evap-

oration from the water surface; but, if the film is aged for 20 hours at zero pressure and then compressed to 47 dynes per centimeter, it is almost completely permeable. They concluded that the increased permeability results from association of the single molecules in the uncompressed film with double molecules with a hydrophilic alcohol group at each end. The double molecules lie flat on the water surface and the film is more permeable.

Zolin (322) showed that the rate of evaporation depends on the volatility of the given component. Littlewood and Rideal (182) derived a relation between observed values of evaporation coefficients and temperature at the evaporating surface. On this basis they explain the wide range in the experimental results.

The shape of the molecules that make up the surface film (3) is important in determining the rate of evaporation. Woog (320) studied the effect of shape in stearic, palmitic, and oleic acids and his results confirmed those of Langmuir (177). The effect of chemical structure on the water-vapor permeability of thin films was evaluated by Weitzel and others (314-317). They found that increased length in the hydrocarbon chain of the fatty acids decreased permeability and that the steric interference of a side chain increased permeability; 8-methylpalmitic acid permitted a 98-percent passage of water vapor, whereas palmitic acid permitted only a 46-percent passage. Films formed by long-chain alcohols showed a similar decrease in permeability with increasing chain length. The steric hindrance was demonstrated by the use of esters. The permeability of the isomers erucic acid (*cis*) and brassidic acid (*trans*) was measured. Brassidic acid greatly retarded the passage of water vapor, whereas erucic acid had little effect.

Harkins (135) found that, when polar compounds are added, the molecules at the interface are oriented with their polar groups toward the solid and their nonpolar groups toward the liquid. Durham (106) concluded that fatty acids with main chains longer than C_{18} make brittle solid films on substrates containing calcium ions at pH 7.5. Others (18, 105, 164, 220, 246) have studied the effects of molecules of different shapes on the rate of evaporation.

Ionization in fatty-acid monolayers on pure water has been studied by Betts and Pethica (54) and Sanders and Spink (257). The surface potentials of spread monolayers of weak acids or bases vary with their pH. This variation may be used to calculate the intrinsic ionization constants of the film forming molecules.

The variation in the solubility of monomolecular films with surface pressures was studied by Sebba and Briscoe (262). The surface pressure exerted by a film, in equilibrium in excess of the solid film forming substance, is not constant but varies with time. They

studied the following film forming materials: cetyl alcohol, octadecyl alcohol, cholesterol, proteins, and stearic, palmitic, oleic, elaidic, brassidic, and erucic acids. Dervichian (92) determined the film pressures, film potential compression at various temperatures, and dipole moments of several monomolecular layers. Harkins and Boyd (136) studied the effect of pressures and temperatures and the detection of phase transitions in monolayers for pentadecylic, palmitic, margaric, stearic, nonadecanoic, and arachidic acids at surface pressures of 0-28 dynes per centimeter and viscosities of 3×10^{-4} to 1 surface poise. They (137) also analyzed the interpretations of Dervichian.

Nutting and Harkins (224) measured the pressure-area relation of monolayers of fatty acids with 14 to 20 carbon atoms at 25°C. and straight-chain alcohols with 14 to 18 carbon atoms at 20°C. The pressure of the transition point, liquid to plastic solid, increases from 6.2 dynes per centimeter for 14 carbon chains to 12.2 dynes per centimeter for 18 carbon chains in the alcohol at 20°C.; the corresponding change for the acids at 25°C. is from 21 dynes per centimeter for 15 carbon chains to 20 dynes per centimeter for 19 carbon chains.

Rosano and LaMer (253) investigated the effect of employing monolayers of C_{17} , C_{18} , C_{19} , and C_{20} members of the saturated fatty-acid series on evaporation. They found that evaporation was independent of the surface pressure of these monolayers in the range 10-24 dynes per centimeter if the film was spread initially under pressure to prevent the entrance of impurities. They measured the surface area, the resistance to evaporation, and the surface viscosity for each substance as a function of the surface pressure. Shishakov (268), in his paper "Electronography as a method for the physical chemistry of surface film," gives an annotated bibliography. Others (34, 35, 91, 110, 143, 160, 167, 200, 201, 202, 205, 211, 242, 243, 256, 286, 302, and 314) have studied the effects of surface pressure and surface tension on evaporation.

Viscosity of monomolecular films was studied by Joly (156-159) and others (67, 93, 94, 111, 138, 254). Joly investigated films of palmitic acid, oleic acid, and tricaproin and drew conclusions about the arrangement of their carbon chains that explain the increase in viscosity with molecular area. The viscosity measurements can give precise information on the equilibrium form of the molecules, the forces of molecular interaction, and the energetics of surface phenomena. He listed 120 references.

The effect of monolayers on the rate of evaporation has been investigated by many men (119, 142, 143, 144, 176, 214, 243, 264, and 265). Archer and LaMer (45, 46) studied the resistance to evaporation of monolayers

of 4 fatty acids of 17, 18, 19, and 20 carbon atoms. Their measurements indicated that the monolayers decreased the rate of evaporation of water by a factor of about 10^4 . Baranaev (48) found that the ratio of evaporation of pure and film-covered water could be expressed by the equation, $V = e - aF_0/T$, where T is temperature and values of a and F_0 were given in dynes per centimeter. Values of a and F_0 were obtained as follows: cetyl alcohol, 55.0, 40; hexadecyl acetate, 53.4, 34; palmitonitrile, 53.0, 13.5; palmitic acid, 52.0, 10.0; stearic acid, 54.2, 6.0; lauric acid, 26.9, 20.0; and oleic acid, 17.1, 29.0. Baranaev (48) derived a formula on the assumption that evaporation takes place through "holes" in the monolayers.

Bartlett and Poulter (51) studied the influence of surface tension on the rate of evaporation of water through surface films. Kheinman's (163) studies indicate that cetyl alcohol decreases the rate of evaporation. A 0.5N solution of sodium oleate has no effect; but, when excess solid sodium oleate is present, evaporation is decreased. Paraffin has no effect, but crude petroleum has. Glazov (122, 123) determined the rate of evaporation for several surface-active substances. He found that a monomolecular layer of cetyl alcohol causes the largest decrease in evaporation when compared with the effect of aliphatic acids, aromatic amines, and other surface-active substances.

The early investigators considered that all surface films were either oils or monomolecular layers; however, a better classification would be oils, multimolecular layers, and monomolecular layers.

Early investigations (48, 50, 122, 176) of monomolecular films have shown that cetyl alcohol has the greatest resistance to evaporation. Docking and others (97) found in their experiments that cetyl and octadecyl alcohol reduced evaporation, and these authors were the first to apply the film on ponds and reservoirs for the control of evaporation. They studied the effects of some multimolecular films which were not successful during field experiments.

Mansfield (192) in 1953 experimented with flakes of cetyl alcohol on reservoirs but found them to be unsuitable. The East African Industrial Research Organization (107) describes a method for pelletizing cetyl alcohol. Mansfield (193, 195) used the pellets successfully in his laboratory and field tests during the 1954-55 season. He placed alcohol pellets in a small raft covered with wire gauze. The initial dosage was estimated to be 3 to 5 pounds per acre. Heath (140) in his article describes the standard method of pelletizing cetyl alcohol.

Laycock (179) used small wood rafts to dispense pellets of cetyl alcohol at the rate of 1 pound per acre to form a thin film that reduced evaporation from 50

to 70 percent. He found that the method is harmless to fish and other animal life but that it inhibits development of mosquito larvae. Downing and Melbourne (99) studied the effect of hexadecyl alcohol on natural waters and found that it reduced the rate of solution of oxygen. They suggested that

in the development of the use of cetyl alcohol, due regard should be given to this potential effect, particularly where reservoirs contain high concentrations of organic matter, the decay of which could create a high oxygen demand.

Boon and Downing (63) found that the efficiency of hexadecyl alcohol in reducing evaporation depends on intensity of solar radiation, wind velocity, relative humidity, the rate at which films are replaced, and biological action.

Grundy (126) studied the use of kerosene for dispersing cetyl alcohol. He found

success in the use of the solution depends on wind, even a light breeze, to carry drops of the liquid over the water surface. The principle by which the film is spread is as follows: when some of the solution is poured on a water surface, it breaks up into drops. The first drops disperse rapidly to spread a film as much as 100 feet from the point of dosing. Additional drops of solution will not disperse in the presence of a film but are carried down wind to areas of water surface with no film, where they in turn disperse. This process is repeated across the reservoir if enough solution is used. The solution damps small waves, so the progress of the spreading film can be observed visually across the reservoir.

He found that evaporation was reduced 20 percent by a dose of 1 liter of solution per day on a 1-acre reservoir. A second experiment on a 5-acre reservoir dosed with 3 liters per day and wind velocities as much as 15 miles per hour showed a reduction in evaporation of slightly more than 30 percent.

McArthur and Durham (189) believe that the use of a mixture of cetyl and stearyl alcohol is more effective than cetyl alcohol alone in reduction of evaporation of water from reservoirs in hot climates. They found that the addition of 5-8 percent of oleyl alcohol improves the spreading and recovery rates, but spreading agents, such as octanol or Pluronic F68, are unnecessary and greatly reduce the effect of the film.

Several organizations in the United States have been studying evaporation suppression. The following have reported on their progress: Southwest Research Institute (101, 102, 103, 169, 249), the U.S. Bureau of Reclamation (77, 291, 292, 293, 307, 308, and 309), the U.S. Geological Survey (133, 134), and others (248, 276, 277).

The Southwest Research Institute began studies in 1955. Dressler (100, 103) used an insulated metal trough filled with water whose temperature was kept

at 30°C. Eighteen battery jars containing distilled water were placed in the trough. He left one or more jars untreated as a control. Dried air was blown over the jars at a rate of about 0.1 mile per hour. Water levels were maintained and replenishment was measured to determine evaporation loss. He studied about 150 potential evaporation retardants and found that hexadecanol and octadecanol gave good results. The U.S. Geological Survey (132) measured evaporation from a 3-acre ranch pond near Southwest Research Institute, both with and without a film.

The U.S. Bureau of Reclamation and U.S. Public Health Service studied evaporation suppression on Kids Lake in 1956 (293) and found that hexadecanol did not affect the water quality, including taste, odor, color, and toxicity. From this they concluded that it was feasible to treat Lake Hefner. Berger (53) studied the effects of hexadecanol and found that it was not toxic to fish and did not create problems for water treatment processes. Timblin (291) worked out a series of indicator oils which shows the presence and degree of compression of a monomolecular layer. A modified method used talc-powder (205) as an indicator for detection on small areas. The Bureau of Reclamation reported reduction in evaporation losses of as much as 65 percent in field studies on Rattlesnake Reservoir (77, 292) in Colorado.

The Bureau of Reclamation (307-309) studied the effect of surface tension on the flotation of small beads hexadecanol, screening tests on monolayers and duplex films, and other properties of monomolecular layers. Ludzack and Ettinger (186) studied the biological oxidation of hexadecanol under laboratory conditions and reported measurable consumption of the material with all substrates tested. LaMer and Robbins (170, 173) have studied the effects of solvents in the spreading of monolayers. The Geological Survey is searching for a suitable solvent.

A significant part of our water supply is lost through evaporation; Meyers estimates the annual evaporation loss in 11 western States is 11.5 million acre-feet (210) and the total water use of the same States amounts to 111 million acre-feet. Dressler (78) found that monomolecular films are especially suitable for the large western reservoirs. He estimated that

the cost, including chemicals, amortization of equipment, labor, and power, totals \$4.50 per acre-foot of water saved, or 1.4 cents per 1,000 gallons, operating 180 days per year. This compares with values of about \$6.00 per acre-foot for irrigation water and \$10.00 to \$40.00 per acre-foot for municipal water.

Dressler thinks that 40 percent of the water normally lost by evaporation could be saved.

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