Evaporation Retardants: Application by Means of a Water-Soluble Matrix

Abstract. *Evaporation retardants interspersed in a solid or semisolid matrix of water-soluble material allow discrete particles of retardant to be released at a controlled rate as the matrix dissolves. This system permits the continuous application of evaporation retardants to a water surface without the use of mechanical devices.*

Monomolecular long-chain alkanol films for reducing evaporation from water surfaces have been little used, owing to lack of satisfactory application systems (*1*). Mechanical devices for applying dusts, molten sprays, emulsions, suspensions, and solutions become clogged, cost too much, or require frequent attention. Aerial spraying and boat-mounted dusters do not provide a continuous supply of alkanol to replace that blown away by wind. Floating boxes of wire mesh containing alkanol flakes or pellets fail because the alkanol and the wire mesh become coated with dust, algae, and bacterial crusts. These application problems have been amply described and discussed in the literature.

I have recently found that long-chain alkanols can be applied to water surfaces at a continuous, controlled rate by interspersing them in a matrix of a material which dissolves when placed in water. As the matrix material dissolves, discrete particles of alkanol are released to form an evaporation-retarding film on the water surface. Particle release rates can be controlled by varying the matrix-alkanol formulation, by varying the surface area exposed to water, or both. Alkanol particle size can be controlled in the preparation process, and spreading agents and bacteriocides can be incorporated in the matrix material. Examples of matrix-alkanol (MA) mixtures and film release rates are given in Table 1.

Matrix materials tested included sugar syrups, gum tragacanth, hydroxyethyl cellulose, gelatin, and bentonite. The alkanol was a commercial-grade mixture containing about 29 percent of hexadecanol, 63 percent of octadecanol, and 8 percent of other alkanols. Gelatin and bentonite interfered with film spreading and were discarded. The saccharides tested did not react unfavorably with the alkanol and could easily be formulated to release alkanol and form surface films.

Film release rates were measured on tap water at 25°C in a plexiglass tray 17.5 by 60 cm, with talcum powder being used as an indicator. A piece (0.1 g) of MA was placed in one end of the tray and the film spreading rate was measured after initial coverage of a 175-cm^2 area. All mixtures except No. 3 were floated or suspended at the water surface. Number 3 rested on the tray bottom and released 40- to 70-μ diameter alkanol particles which floated to the water surface to produce a film at the rate of 440 cm^2 min^{-1}. Film release rates varied from 50 to 3800 cm^2 min^{-1}. Mixture No. 6 had alkanol particles of 15- to 25-μ average diameter and contained a quaternary ammonium chloride surfactant. Both small particle size and the surfactant probably contributed to the high spreading rate. Mixture No. 5, without a spreading agent and with 150- to 200-μ particle size, produced film at a rate of 3030 cm^2 min^{-1}. Particle size was measured by observation with a microscope and calibrated grid. Particles in mixtures No. 3 and No. 6, prepared with molten alkanol, were spherical. Particles in mixtures Nos. 1, 2, 4, and 5, prepared with unmelted powdered alkanol, were highly irregular and somewhat crystalline in appearance.

Table 1. Matrix-alkanol formulations and film-release rates.

Mix No.	Matrix material		Alkanol		Mixing temp. (°C)	Film release (cm^2 min^{-1})
	Type	Amt. (% by wt.)	Amt. (% by wt.)	Particle size (μ)		
1	Glucose syrup, sp. gr. 1.39	64	36	150–200	24	50
2	Gum tragacanth, 2% gel	61	39	150–200	24	250
3	Sucrose syrup, sp. gr. 1.47	71	29	40–70	60	440
4	Glucose syrup, sp. gr. 1.32	53	47	150–200	24	1700
5	Hydroxyethyl cellulose, 4% gel	70	30	150–200	24	3030
6	Sucrose syrup, sp. gr. 1.40	73*	25	15–25	60	3800

* Plus 2 percent alkyl quaternary ammonium chloride emulsifier.

Alkanol particle size is important because of its effect on rate of film formation and on particle buoyancy. All other things being assumed equal, decreasing particle size increases the alkanol-water surface contact area per unit of alkanol and thereby increases the rate of film formation. On the other hand, decreasing particle size decreases particle buoyancy. Very small particles released beneath the water surface may not rise to form a film. Some compromise in particle size is necessary. Individual alkanol particles of 150- to 200-μ average diameter dispersed into film in less than 2 seconds, as observed visually, and they were small enough for rapid film formation. Particles of this size and the 40- to 70-μ particles from mixture No. 3 readily floated to the surface and formed a film when released beneath the water surface. The 15- to 25-μ particles from mixture No. 6 did not rise to the surface when released under water and it was necessary to float mixture No. 6 on the water surface to obtain a film. This failure to rise is not understood since 20-μ spherical particles with a density of 0.873 g cm^{-3} should theoretically rise at a rate of about 5 cm hour^{-1}. Possibly the surfactant changed the effective volume-density relation.

Alkanol particle size can be controlled during the formulation process. The simplest method is to mix powdered alkanol, ground to the desired size, into matrix materials at temperatures below the melting point of the alkanol. When formulations are prepared with melted alkanol, the particle size can be controlled by temperature and mixing shear. Mixing molten alkanol into matrix material maintained at a temperature just below the melting point of the alkanol produces larger particles than those obtained when both materials are at temperatures above the alkanol melting temperature. Similarly, high-smear mixing produces smaller particles than low-shear mixing. Surfactants can also be used to reduce particle size in mixtures prepared with molten alkanol.

Rate of particle release from the matrix can be controlled by both formulation and exposure of the MA mixture. Release rate is dependent upon the basic matrix material, its concentration, and the amount of alkanol added. At equal concentrations, hydroxyethyl cellulose gel dissolves faster than gum tragacanth gel. For a given matrix material, the rate of dissolving increases with decreasing concentration. A 2-percent gum tragacanth gel dissolves more rapidly than a 4-percent gel. For a given quantity of matrix at a given concentration, the rate of particle release can be changed by varying the amount of alkanol added to the mixture. Rate of particle release is also dependent on the area of MA mixture exposed to the water. There are several possibilities for maintaining a relatively constant exposure area. A simple and effective method involves placing the MA mixture in a cylindrical container which is open at one end.

Evaporation reduction with MA mixtures No. 6 and No. 3 was tested in June 1964 on outdoor water tanks (274 cm in diameter by 91 cm deep). The tanks were set in the ground with the tops approximately flush with a surrounding grass lawn. Untreated evaporation rates were about 7.2 mm day^{-1}. About 50 g of MA mixture No. 6 was suspended at the water surface with a small float. This treatment reduced evaporation about 50 percent for a 2-day period. During the test, wave action disintegrated the material. To reduce disintegration by wave action, mixture No. 3 was placed in a test tube (2.2 by 17 cm). The tube was suspended from a float with the open end about 0.5 cm beneath the water surface. Over a 2-week period, alkanol particles were released at a reasonably constant rate of about 0.5 g alkanol per day. Evaporation was reduced about 40 percent with this treatment. This reduction was accomplished in spite of a heavy film of dust and algae on the water surface. Indicator oils showed that this dust and algae film could not be displaced until alkanol film pressures exceeded 30 dynes cm^{-1}.

The MA mixtures can be applied to water surfaces from floating or sunken containers and the containers can be placed from shore, boats, or aircraft. Alkanol release rates can be adjusted to suit average wind conditions. The resulting application of excess alkanol during periods of calm may be a problem on large surfaces of water but will not be a problem on small surfaces where the total cost of alkanol is low. Thus, dispersion of long-chain alkanol in a water-soluble matrix is a promising method for applying monomolecular films to reduce evaporation from small ponds and reservoirs. Additional study and development may show the method to be of value in reducing evaporation from large reservoirs.

LLOYD E. MYERS
U.S. Water Conservation Laboratory,
Route 2, Box 816-A,
Tempe, Arizona 85281

References and Notes

1. *World-Wide Survey of Experiments and Results of the Prevention of Evaporation Losses from Reservoirs*, International Commission on Irrigation and Drainage, New Delhi, India (1960); R. R. Cruse and G. E. Harbeck, Jr., *U.S. Geol. Surv. Water Supply Paper No. 1480* (1960); "Present status of evaporation reduction by chemical films," Miscellaneous Paper No. 5-475, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi (1962); V. K. La Mer, Ed., *Retardation of Evaporation by Monolayers: Transport Processes* (Academic Press, New York, 1962); "Survey of methods for evaporation control, task group report," *J. Am. Water Works Assoc.* **55**, 2 (1963); G. E. Koberg, R. R. Cruse, C. L. Shrewsbury, *U.S. Geol. Surv. Water Supply Paper No. 1692* (1963).

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Cationic Glass Electrode Response in Aqueous Solutions of Sodium Chloride and Potassium Chloride

Abstract. *The selectivity of glass electrodes suitable for potassium-ion measurements depends on the age of electrodes and the composition of the solution. An empirical equation describing the electrode potential as a function of solution composition is given for practical application in solutions containing both sodium and potassium.*

Glass membrane electrodes have been used for the determination of sodium and potassium ion activities in biological and mixed-ion solutions (*1*, *2*). Eisenman, Rudin, and Casby (*3*), in their original description of cation-selective electrodes, developed an empirical equation relating electrode potentials to cation activities in mixed-ion solutions. In its general format this equation implicitly predicted variations in bi-ionic selectivities, that is, how well an electrode "sees" one cation in preference to another. The equation is cumbersome, however, and difficult to apply to practical problems in the analysis of mixed solutions except in the limiting case of $n = 1$. It is therefore not surprising that in most experiments with such electrodes the selectivity of a given electrode for a specific cation has been assumed to be a constant.

In the application of these electrodes to biological solutions having widely different sodium and potassium concentrations, significant errors in potassium analyses may result from the foregoing assumption. An empirical equation, suitable for practical application, has therefore been derived to include variable electrode selectivity as a function of solution composition.

Capillary electrodes (*4*) (1 mm in outside diameter) of potassium selective (NAS_{27-4}) glass (in moles percent: Na_2O, 27; Al_2O_3, 4; SiO_2, 69) were used. The electrode format and associated measuring equipment have been described (*2*). All activity (a_{K^+}) measurements were made at *p*H 7 and at 25° ± 2°C. Standard solutions were made from appropriate chloride salts (reagent grade). Electrode-potential measurements in all experimental solutions were

Table 1. Data for unaged NAS_{27-4} electrode. All activities and concentrations are milliequivalents per liter.

$(a_{K^+})_{std.}$	$[Na^+]$	$[K^+]$	$\frac{[Na^+]}{[Na^+]+[K^+]}$	γ_{NaKCl}	a_{Na^+}	a_{K^+}	$\Delta E/S$	k_{KNa}
9.0	200	5	0.98	0.732	146.4	3.66	+0.393	0.127
9.0	50	5	.91	.812	40.6	4.06	+0.054	.151
9.0	5	5	.50	.902	4.51	4.51	−0.222	.196
77.0	200	50	.80	.718	143.6	35.9	−0.119	.160
77.0	50	50	.50	.774	38.7	38.7	−0.215	.213
77.0	200	200	.50	.669	133.8	133.8	+0.326	.219
77.0	50	200	.20	.702	35.1	140.4	+0.297	.342