Open-air evaporimeter studies on the water evaporation reduction due to hexadecyl (cetyl) alcohol, octadecoxy-ethanol and other monolayers

A. V. DEO, K. V. GEORGE, N. R. SANJANA, S. B. KULKARNI and M. K. GHARPUREY

National Chemical Laboratory, Poona

(Received 3 December 1962)

ABSTRACT. Monomolecular films of cetyl and other n-long chain alcohols, n-octadecoxy and other ethanols, and their mixtures, which in earlier laboratory experiments were found to be effective in reducing evaporation from water surface were tested in the open air in evaporimeters and small ground level brick-cement lined tanks. The results of these experiments are reported. It was found that the alkoxy-ethanol monolayers were more effective than the alcohols. The results are discussed in the light of the known physical properties of these substances, especially as monolayers.

1. Introduction

During the last decade, there has been tremendous interest in water conservation by spreading on water surface certain insoluble monomolecular films which act as water evaporation retardants. In the early experiments Mansfield (1953) and co-workers were successful in obtaining a sizable reduction in water evaporation from small tanks with cetyl alcohol films. Later, in this country among others, mixtures of cetyl and stearyl alcohol were found to be more effective than cetyl alcohol alone, especially at higher ambient temperatures.

It was observed that even though in the laboratory experiments cetyl alcohol gave reductions as high as 40—60 per cent, in field trials its performance was not always as good, and sometimes was rather poor (Lake Hefner Report, 1958). The possibility of any alternative compound which should prove more effective than cetyl alcohol was, therefore, examined in this laboratory.

From a monolayer spread on the water surface there are continuous losses of the film molecules due to: (a) dissolution into the underlying water (e.g., cetyl alcohol is to a certain though limited extent soluble in water; solubility—1 in $10^9$ parts—Sutherland 1957); and (b) evaporation of the film forming molecules into air (Brooks and Alexander 1960). The value of the film pressure obtained will, therefore, be less than the equilibrium value if the net rate of loss is not inconsiderable compared to the rate of spreading.

Under field conditions there are three more possible reasons for film loss: (c) film collapse due to the blowing of wind and due to water waves. Wind pushes the film to the leeward side where it will collapse due to the build-up of excessive surface pressure. Waves also will cause local transient pressure build-up and also may fold the film over. This collapsed film could carry over some water molecules between its folded-up double layers and thus may not respread as easily as a fresh solid speck (Cary and Rideal 1925); (d) deposition on to the leeward side of the reservoir (the multilayer build-up) due to the waves; and (e) decomposition of the film molecules brought about by biological factors. Therefore, under field conditions, the film pressure rarely approaches the equilibrium value.

*Communication No. 553 from the National Chemical Laboratory, Poona
It is thus seen that in order to overcome these losses the rate of spreading should be large. Now the rate of spreading appears to be indirectly related to the melting point in that related compounds with higher melting point spread at lower rate (Deo et al. 1962). This rules out the use of the higher homologues of cetyl alcohol in the field, even though in the laboratory experiments films of these show higher resistance to evaporation (Deo et al. 1961).

With the above in view, various possibilities were considered, and it was decided to try compounds formed on condensation of one ethylene oxide molecule \((\text{H}_2\text{C}-\text{O} \cdot \text{CH}_2)\) with cetyl alcohol and its higher homologues such as octadecyl alcohol. Actually these compounds were synthesised by reacting pure long-chain bromide with monosodium glycolate. \(\text{C}_n\text{-Br} + \text{Na} \cdot \text{OC}_2\text{H}_4\text{OH} \rightarrow \text{C}_n \cdot \text{OC}_2\text{H}_4\text{OH}\). The film forming properties of these \(n\)-alkoxyethanols \([\text{CH}_2-(\text{CH}_2)_{n-2} \cdot \text{CH}_2 \cdot \text{OCH}_2 \cdot \text{CH}_2\text{OH}\) or \(\text{C}_n \cdot \text{OC}_2\text{H}_4\text{OH}\) were studied in the laboratory. It was found that these compounds had lower melting points, higher rate of spreading, higher equilibrium film pressure than the corresponding alcohols, and their films exhibited higher resistance to water evaporation (Deo et al. 1960, 1961, 1962).

Therefore as a prelude to their field use, it was thought worthwhile to test these compounds in the open on a semifield scale using evaporimeters and small tanks.

2. Experimental

These studies were carried out in the open in three types of experimental set-ups.

(i) On 8' diameter evaporimeter pans using lake water,

(ii) On 4' diameter evaporimeter pans in the laboratory garden area using water from municipal filters, and

(iii) On ground level 25' \(\times\) 6' brick-cement lined tanks using lake water.

The evaporimeters were connected to smaller (1' diameter-Athavale type*) vessels with spherometer arrangement for reading the water level. The ground level tanks had still-wells and book-gauge arrangement for measuring changes in height of water level due to evaporation.

The evaporimeters, at the start of each experiment, were filled with fresh water and made to overflow in order to remove surface impurities. At this stage, a small quantity of the solution of the film-forming material was added which aided in the removal of the surface impurities. The level of water was then brought down to a predetermined value about 1-2" from the top. At these levels, the evaporimeters gave the same evaporation through clean water surface. More solution was then added.

Subsequent addition of water was carried out through a funnel with the stem dipping into water well below the surface. In this way the film was not unduly disturbed by the water added.

Since the water surface in the ground level tanks could not be cleaned by overflowing it was swept with clean muslin, and then the solution added.

Five per cent solutions made in white petrol were normally used. In some experiments more solution was added every morning for replenishment. In others, the durability of the films was tested by observing the day-to-day fall in the film efficiency.

The water level readings were normally taken in the morning after a 24-hour interval. The per cent evaporation reduction was calculated from the difference in evaporation from the clean and the film-covered water surface in the neighbouring pans.

3. Results

3.1. 8' diameter evaporimeter pans—Since only two pans were available, only one compound could be tested at a time, the second pan being used as control. A number of experiments were, therefore, repeated on the behaviour of the films of hexadecyl alcohol \((\text{C}_{16} \cdot \text{OH})\) and octadecyl-ethanol \((\text{C}_{18} \cdot \text{OC}_2\text{H}_4\text{OH})\).

Fig. 1 shows the best results of reduction due to the above two films and C_{16}-OC_{2}H_{4}OH. The lowest results of C_{18}-OC_{2}H_{4}OH film were much better than the best results due to the C_{16}-OH. The lowest values due to C_{16}-OH came to only 20 per cent reduction on the first day. Since in both these experiments the solution was added at the beginning of the experiments only, the area under the two curves may be taken as a rough measure of the relative overall efficacy of the two films. The two areas are in the ratio C_{18}-OC_{2}H_{4}OH : C_{16}-OH as 4 : 1.

It would be interesting to see how the evaporation retardation would vary with the chain length of the film-forming compound. In this connection two experiments on films of hexadecoxy-ethanol (C_{16}-OC_{2}H_{4}OH) gave results similar to cetyl alcohol (Fig. 1). On the other hand, experiments with films of octadecyl alcohol indicated a poor reduction as a result of spreading difficulty.

At present, films of equimolar mixture of hexa and octa-decyl alcohols are being tried on a large scale under conditions of high ambient temperature. A mixed film of equimolar hexa- and octa-decyl alcohols (C_{16}-OH+C_{18}-OH) was, therefore, examined. This gave (Fig. 2) better reduction than hexadecyl alcohol alone though its performance was not as good as that of hexadecoxy ethanol. Apparently the admixture of C_{16}-OH with C_{18}-OH reduced the spreading difficulty of the latter, while the incorporation of the longer chain molecules, viz., C_{18}-OH in the monolayer, gave rise to better retarding efficiency than pure C_{16}-OH monolayers.

Mixed 3:1 (Fig. 2) and 1:3 molar films of pure cetyl and behenyl alcohols (C_{16}-OH+C_{27}-OH) did not give reductions as good as those given by the above C_{16}-OH+C_{18}-OH mixture. Thus, incorporation of C_{16}-OH in the still higher homologue (C_{22}-OH) did not appear to reduce the spreading difficulty of the higher homologue to a sufficient extent.

In the initial experiments, there was vigorous mossy growth on the water surface in the evaporimeters, so that every day growth covering areas as large as one sq. ft had to be removed. The tendency for these growths was found to be considerably reduced if the water was filtered through two-fold muslin.

3'2. 4' diameter evaporimeter pans using filtered water—The supply water came through a sand-bed filter and treated with alum and chlorine. The chlorination would be expected to reduce the film decay due to biological decomposition and should thus make the film more durable. In fact this was observed. Since four evaporimeters of this type were available, two compounds could be simultaneously studied, the two pans being used as control. The comparative behaviour of C_{18}-OC_{2}H_{4}OH and C_{16}-OH is shown...
in Fig. 3. The superior evaporation retarding behaviour of the former is evident. Fig. 4 shows the comparative behaviour of $C_{18}$- and $C_{16}$-$OC_{2}H_{4}OH$. Here again the decidedly superior behaviour of the former compound with its longer chain length is noticeable. Further more, $C_{16}$-$OC_{2}H_{4}OH$ appears to be superior to $C_{16}$-$OH$. In general it was found that films containing molecules with $-OC_{2}H_{4}OH$ group were more durable than the alcohol films.

The monolayer films were found to be more durable in the 4' diameter pan experiments with filtered water than in the other two set-ups (8' pans and ground level tanks). In fact it was very frequently observed that over a period of one week, films of the alkoxy ethanol or alkoxy ethanol and alcohol mixtures did not lose their efficiency. The alcohol films or alcohol and ester mixture films, on the other hand, did exhibit deterioration during this period.

3.3. 25' x 6' brick-lined ground-level tanks—
These were a group of four rectangular tanks in one row. The experiments on these tanks gave rather larger variations in evaporation since in these experiments the water surface was not cleaned by the overflow technique and also since due to the dusty condition of the surroundings, the surface could not be kept clean for even short periods. Here also a large number of experiments were carried out for comparing the efficiency of cetyl alcohol and octadecyloxy-ethanol films. In all these it was found that the efficiency of the $C_{18}$-$OC_{2}H_{4}OH$ film was invariably better than that of cetyl alcohol by 20 on the per cent evaporation reduction axis (see Fig. 5).

In a number of experiments, the efficiency of a film of an equimolar mixture of $C_{18}$-$OH + C_{18}$-$OC_{2}H_{4}OH$ was compared with that of $C_{16}$-$OH$. The chief reason for doing this was that during the condensation of ethylene oxide with $C_{18}$-$OH$ to obtain $C_{18}$-$OC_{2}H_{4}OH$, some of the alcohol may remain unreacted. The films of $C_{18}$-$OH$ as such are rather ineffective, since this compound spreads with difficulty. It was found that the $C_{18}$-$OH + C_{18}$-$OC_{2}H_{4}OH$ mixture films were more efficacious as compared to those of cetyl alcohol. Obviously, the mixture was exhibiting lesser spreading difficulty than $C_{18}$-$OH$, which is in accord with the results of laboratory experiments.

It is known that wind creates a drag on the water surface as a result of which the monolayer tends to be carried over to the leeward side where, as a result of pressure build-up it collapsed. Two preliminary experiments were made in order to see if this action could be partially rectified.

(i) It has been reported (Ries and Walker 1961) that the incorporation of polyvinyl acetate in a $n$ long chain carboxylic acid
monolayer considerably increases its collapse pressure, while it has no effect on the collapse pressure of a $n$-long chain alcohol film. The behaviour of films of the composition (cetyl alcohol : palmitic : polyvinyl acetate = 80 : 20 : 5) was, therefore, compared with that of pure cetyl alcohol film.

(ii) The overall motion of the water surface as a result of the wind drag would be hindered by a surface barrier, e.g., of polythene. The effect of such a barrier on the evaporation reduction through cetyl alcohol films was also studied.

Both the above methods indicated a slight positive effect on the evaporation reduction. However, the experiments had to be stopped due to the onset of the monsoon.

In another communication (Katti et al., 1962) it is reported that monolayers of a variety of substances and of their mixtures exhibited far better evaporation reduction during eight hours of mid-day time (9 AM to 5 PM) than during the remaining sixteen hours of cooler ambient temperature. This was confirmed with a few experiments on he ground level tanks as well as 8' evaporimeter pans.

4. Discussion

The above experiments were conducted in order to test the efficacy of the alkoxyethanol monolayers, especially of $C_{16}-OC_2H_4OH$, and to compare it with that of the alcohol monolayers especially $C_{16}-OH$, under a variety of semi-field conditions. Due to a number of uncontrollable variables such as the ambient temperature, the wind velocity, the dust falling on the monolayer surface, and other contaminating impurities in the surface, variations were observed in the values obtained for the reduction in evaporation. Therefore, a large number of repetitive experiments were carried out, from which certain definite trends as presented above could be discerned.

It was thus observed that (i) a film of octadecoxy-ethanol ($C_{16}-OC_2H_4OH$) consistently exhibited a much superior water evaporation retardation than cetyl alcohol, or $C_{16}- + C_{18}-OH$ equimolar mixture films, (ii) the alkoxy-ethanol films were more durable than the alcohol films, (iii) on filtered water surface, their efficiency remained unimpaired over a period of one week.
while on (unfiltered) lake water surface, the alkoxy-ethanol films also showed loss in efficiency with time, (iv) however, under similar conditions the alcohols films decayed much faster.

5. Acknowledgements
Thanks are due to Dr. D. G. Kulkarni, Soil Survey Officer, P.W.D. of the Government of Maharashtra, Bombay, for facilities and loan of evaporimeters. Thanks are also due to Mr. M. S. Wadia, of the Organic Chemistry Division, for the preparation of octadecoxy-ethanol.

REFERENCES

Deo, A. V., Kulkarni, S. B., Gharpurey, M. K. and Biswas, A. B. 1961

Mansfield, W. W. 1953
Ries, H. E. and Walker, D. C. 1961
Sutherland, K. L. 1957

UNESCO Symposium on water evaporation Control held at National Chemical Laboratory, Poona.

Research, 10. 198.