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Investigation of Some Factors Influencing Isomalathion Formation in Malathion Products¹

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Isomalathion contents of malathion powders prepared with attapulgite, bentonite, Celite, Fuller's earth, kaolinite, and silicate were influenced by the carrier exchangeable cation (Na, K, Ca), surfactant, relative humidity (RH) of the formulation and storage environment, and the container surface. The isomalathion content and the period for attaining its maximum on storage at 55 ± 1 °C depended on the carrier as well as the other factors stated above. The isomalathion formed from malathion applied on plant leaves was below detection level (0.2 ppm) over a period of 14 days.

In 1976 an epidemic of human poisoning from the handling of malathion water-dispersible powder (WDP) was reported from Pakistan (Baker et al., 1978). Investigations by these authors revealed that the mammalian toxicity correlated best with the isomalathion [*S*-methyl isomer of malathion; *O,S*-dimethyl *S*-1,2-dicarbethoxy ethyl phosphorodithioate] content of the powders. Subsequent studies confirmed this and also indicated that the auxiliaries employed in solid malathion formulations induced isomalathion formation in formulations during tropical storage and/or storage at elevated temperatures (Aldridge et al., 1979; Miles et al., 1979).

Systematic information on the effect of solid formulation carriers on the isomalathion content of malathion powders was reported by Halder and Parmar (1984). The isomalathion content varied with each carrier but did not correlate with the physicochemical characters of the carriers such as pH, pK_a , bulk and particle density, cation-exchange capacity, sorptivity, and specific surface area. In order to further understand the factors influencing the content of this isomer, studies on the role of exchangeable cations on the carrier, some surfactants used in water-dispersible powders, relative humidity of the environment (affecting hydration status of carrier and WDP), and the container and leaf surfaces were undertaken.

MATERIALS AND METHODS

Carrier. Industrial-grade attapulgite, bentonite, kaolinite, Fuller's earth (MCA Industries, New Delhi, India), Celite (Loba Chemie, Wien Fishamend, Australanal), silica gel H (Glaxo Laboratories Ltd., Bombay, India), and hydrated calcium silicate (Hindustan Insecticides Ltd., New

Delhi, India) were investigated. Specific surface areas (Carter et al., 1965) (m^2/g): attapulgite, 116.8 (lit. 140; Escard, 1952); bentonite, 575 (lit. 580-750; Raman and Ghosh, 1974); kaolinite, 34.1 (lit. 37-45; Escard, 1952); Fuller's earth, 510 (lit. 500; Halder and Parmar, 1984); Celite, 169.2; silica gel H, 540.6; hydrated calcium silicate, 726.1. The differential thermal analysis of the calcium clay (DTA apparatus, Stanton-Redcraft, alumina reference, heating at 10 °C/min from 40 to 1100 °C in air) showed the following: attapulgite, 100, 570 (lit. 180, 280, 400, 800 (exo); Kulbicki and Grim, 1959); bentonite, 160, 700, 850-950 (S-shaped) (lit. 150, 700, 850-950 (S-shaped); Mackenzie, 1970); kaolinite 570, 1000 (exo) (lit. 550-580, 1000 (exo); Holdridge and Vaughan, 1957); Fuller's earth, 150, 550 (lit. 150, 550-600; Mackenzie, 1970); Celite, 120, 150, 750; hydrated calcium silicate, 80, 730, 875 (exo). The surface area and DTA values indicated that bentonite, kaolinite, and Fuller's earth were of good quality and attapulgite was of doubtful identity. Celite, silica gel H, and hydrated calcium silicate were pure-grade authentic materials, but their surface area and DTA values could not be verified from the literature.

Malathion. Technical-grade malathion (Hindustan Insecticides Ltd., Maharashtra, India), a colorless liquid (96.96%, moisture content 0.03%, acidity 0.15%), was used.

Surfactants. Acipon ADS 1, a mixture of alkyl sulfate, alkyl aryl sulfonates, and some synthetic dispersing agents (Ahura Chemical Products Pvt. Ltd.); Dispersol F Conc. PDR, a powder based on the sodium salt of methylene-bis[naphthalenesulfonic acid] (Indian Explosives Ltd.); Idet 20, a mixture of alkyl aryl sulfonates (Hindustan Insecticides) and sodium lauryl sulfate (Hopkins and Williams), were used.

Preparation of Monoionic Clays. An appropriate quantity of attapulgite, bentonite, Celite, Fuller's earth,

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and kaolinite was worked up to remove soluble salts and organic matter (Jackson, 1956) and iron oxides (Mehra and Jackson, 1960). The clay size fraction ($<2 \mu\text{m}$) was separated by the sedimentation method (Jackson, 1956) and flocculated with NaCl solution. An aliquot of this was washed Cl^- -free, dried (60°C), and ground to obtain sodium clay. Suitable aliquots from the flocculated sodium clay when similarly worked up after treatment with 1 N KCl or 1 N CaCl_2 yielded potassium and calcium clay, respectively (Jackson, 1956).

Isomalathion Preparation. Malathion (10 g) along with 20 g of silica gel (60–120 BSS) was taken up in 10 mL of N,N -dimethylformamide and refluxed on an oil bath at 110°C for 20 min with use of an air condenser. The reaction mixture was cooled and worked up with water (to dissolve N,N -dimethylformamide), and isomalathion was extracted in benzene. The benzene extract was dried over anhydrous Na_2SO_4 ; solvent was removed in a rotatory evaporator at 50°C and purified on a silica gel (300 g) column. Stepwise elution was done with 50 mL of hexane, 800 mL of 2:1 hexane-benzene, 500 mL of 1:1 hexane-benzene, 1000 mL of benzene, and 1500 mL of 2:1 benzene-ethyl acetate, collecting the eluate in 50-mL lots. Fractions showing single spots against reference isomalathion on TLC (Halder et al., 1983) were combined; solvent was removed on a rotatory evaporator at 50°C and stored over fused CaCl_2 at $5-6^\circ\text{C}$ in a vacuum desiccator (yield 50–60%).

Formulation. On the basis of the malathion holding capacity of the commercial carriers or of the laboratory-prepared monoionic clays, to the point of free-flowing powder, the following were impregnated (% w/w): 20 in attapulgite, Celite, and kaolinite; 25 in bentonite and Fuller's earth; 40 in silica gel H; 50 in hydrated calcium silicate. The requisite quantity of malathion was taken in chloroform and added to the carrier clay, worked into a paste by adding more chloroform to ensure thorough impregnation, dried under a current of air at 25°C , and ground to a fine, free-flowing powder. In surfactant studies, surfactant was added at 5% w/w of the formulation to the malathion solution and impregnated on carriers (bentonite, kaolinite, hydrated calcium silicate, silica gel H) as above. Malathion carrier powders served as control.

Effect of Relative Humidity. Desiccators containing saturated solutions of potassium acetate, potassium thiocyanate, or ammonium sulfate in contact with the respective salt, when maintained at $55 \pm 1^\circ\text{C}$, provided relative humidities of 41, 65, and 93%, respectively. Samples (15 g) of each commercial carrier were heated at 110°C for 24 h and cooled in a desiccator over fused CaCl_2 . The carrier samples were then taken in Petri dishes, equilibrated in the humidity chambers for 7 days, impregnated with malathion as described earlier, and put back in the respective humidity chamber for incubation.

Effect of Container Surface. Borosilicate glass (Petri dish diameter 5 cm), aluminum (box diameter 5 cm), and polyethylene (bottle diameter 5 cm) surfaces were studied. Chloroform solution providing 100 mg of malathion was spread at the base of each of the seven containers under each test surface and the solvent evaporated under a ceiling fan to get thin films.

Effect of Leaf Surface. Seven 40-day-old *Vigna radiata* L. plants were marked in the field, and three trifoliate leaves per plant were treated with 3 mL of solution containing 4.65 mg of malathion in 1:2 water-methanol.

Incubation, Sampling, Extraction, and Recovery. In studies on the effect of carrier-exchangeable cations,

surfactants, and relative humidity, a suitable amount (200 mg) was withdrawn from each mixture (0-day sample) and the remaining mixtures were immediately incubated at $55 \pm 1^\circ\text{C}$ for 12–14 days in bakelite screw-capped sample vials. Further samples were periodically withdrawn. Portions of chloroform (3 mL) were added to each withdrawn sample, and the resultant mixtures were stirred intermittently with a glass rod for 1 h and filtered through Whatman No. 42 filter paper under suction. A 1-mL aliquot of the filtrate was taken, the solvent removed on a rotatory evaporator at 50°C , and the residue dissolved in 2 mL of isopropyl alcohol and analyzed for isomalathion content.

In studies on the effect of container surface, one sample per test surface (0 h) was withdrawn for analysis immediately after solvent evaporation. The remaining containers were then incubated at $55 \pm 1^\circ\text{C}$ for 12 days. One container under each surface was periodically withdrawn; the contents were dissolved in 2 mL of isopropyl alcohol and analyzed.

In the studies on plant leaves, one plant (three trifoliate leaves) was plucked per sampling, macerated with 5 g of anhydrous Na_2SO_4 , and extracted in 75 mL of chloroform. The extract was concentrated to 10 mL on a rotary evaporator at 50°C and passed through a cleanup column of charcoal-anhydrous Na_2SO_4 admixture (5 + 5 g) sandwiched between anhydrous Na_2SO_4 (5 g) layers. It was eluted with 50 mL of chloroform and the eluate freed of chloroform on a rotary evaporator. The residue was dissolved in 2 mL of isopropyl alcohol and isomalathion estimated. Isomalathion recovery from the leaves was only 35%, against a recovery of 99% from the clean up column.

Analysis. Isomalathion was analyzed by high-performance liquid chromatography (HPLC). Two instruments, Spectra Physics Inc. Model SP 8000 B, equipped with an integrator and a variable-wavelength ultraviolet (UV) detector, and Kontron analytic liquid chromatograph Series 640, Kontron Electrolab, London, England, equipped with a variable-wavelength UV detector and millivolt recorder, were used. The former employed a Zorbax Si-60, $10 \mu\text{m}$, steel column ($250 \times 4.6 \text{ mm}$), injection volume 10 μL , attenuation 0.16 AUFS, recorder sensitivity 40 mV fsd, and solvent flow rate 1 mL/min. The latter used Lichrosorb Si-60, $10 \mu\text{m}$, steel column ($250 \times 4.9 \text{ mm}$), injection volume 20 μL , attenuation 0.08 AUFS, recorder sensitivity 10 mV fsd, and solvent flow rate 1.2 mL/min. Isooctane-isopropyl alcohol-dichloromethane (9:1:0.05) as eluant, wavelength 222 nm, and chart speed 10 mm/min were common to both. The retention time for isomalathion was around 10 min.

RESULTS AND DISCUSSION

Effect of Carrier Cations. All three cations saturating different clays increased isomalathion contents of the powders as compared to the malathion control (Figure 1). Except sodium attapulgite (1a), calcium Celite (1c), silica gel H, sodium silicate, and hydrated calcium silicate (1 f), all other monoionic clays showed higher isomalathion contents than the prescribed AID/WHO limit (Miles 1979; Miles et al., 1979). On different clays, the relative order among cations on the prescribed 6th day of incubation was

attapulgite	K > Ca > Na
kaolinite	
bentonite	Ca > K > Na
Fuller's earth	
Celite	Na > K > Ca
silicate	Na > H > Ca

Exchangeable K and Ca ions in attapulgite, bentonite, and kaolinite showed higher isomalathion contents as

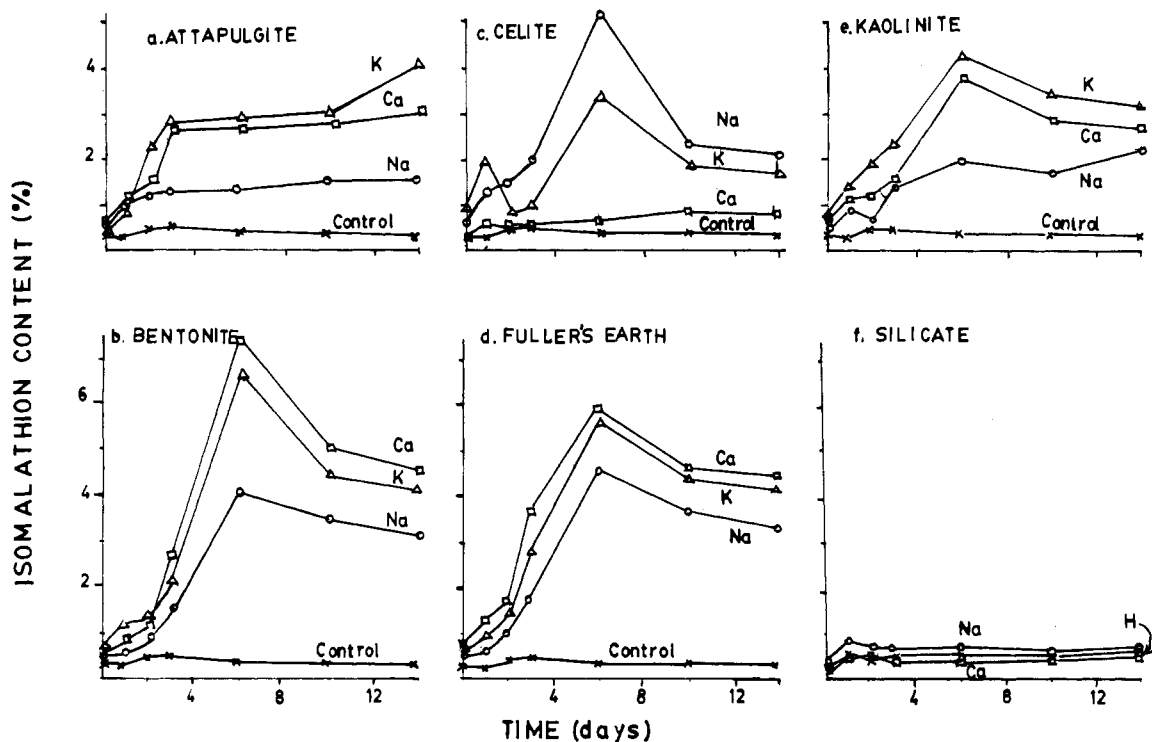


Figure 1. Effect of monoionic clays on the isomalathion content in malathion powders.

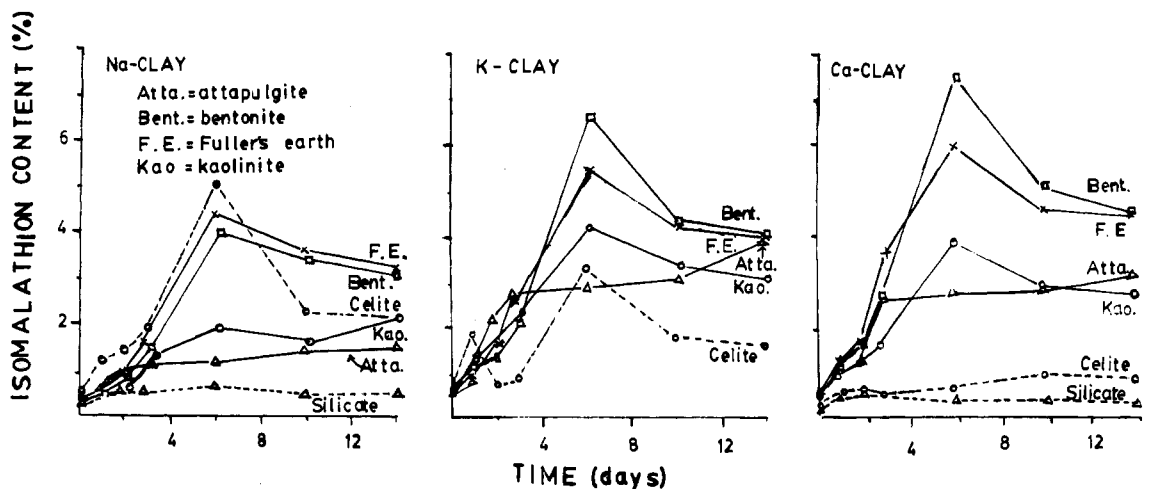


Figure 2. Relative order among the monoionic clays with respect to isomalathion content in the formulated product.

compared to Na. Sodium and potassium ions in Celite caused much higher isomalathion contents compared to calcium ions. Different cations on Fuller's earth and silicate did not show any marked variation among themselves. However, Fuller's earth with all three cations showed higher isomalathion contents in comparison with silica gel H, sodium silicate, and hydrated calcium silicate. In a separate study employing bentonite and kaolinite all the test cations were found to increase the isomalathion content as compared to the corresponding untreated carrier.

For each cation, the order among the clays on the 6th day (Figure 2) was as follows. Sodium clay: Celite > Fuller's earth > bentonite > kaolinite > attapulgite > silicate. Potassium clay: bentonite > Fuller's earth > kaolinite > Celite > attapulgite. Calcium clay: bentonite > Fuller's earth > kaolinite > attapulgite > Celite > silicate.

The period of attaining the maximum isomalathion content varied with the carrier and the cation. It was maximum on the 6th day in bentonite, Celite (except

calcium Celite, 10th day), Fuller's earth, and kaolinite (except sodium kaolinite, 10th day). Attapulgite (except sodium attapulgite, 10th day) recorded maximum on the 14th day. Silica gel H and sodium silicate recorded on the 1st day and hydrated calcium silicate and malathion on the 2nd day. This confirms an earlier observation by Halder and Parmar (1984) that the isomalathion content of powders revealed maxima before as well as after the prescribed 6-day period of storage at 55 °C.

Effect of Surfactants. The effect of surfactants on isomalathion formation in different malathion powders is shown in Figure 3A. Their addition to malathion powders, with the exception of sodium lauryl sulfate addition to bentonite, increased the isomalathion content as compared to the respective control. Malathion-kaolinite powders revealed higher isomalathion contents than that prescribed in AID/WHO specifications when formulated with Acipon ADS 1 or sodium lauryl sulfate. Among carriers, the order of isomalathion formation varied with the surfactant used. On the prescribed 6th day of incubation, the order was as follows. Bentonite: Acipon ADS 1 > Dispersol F Conc.

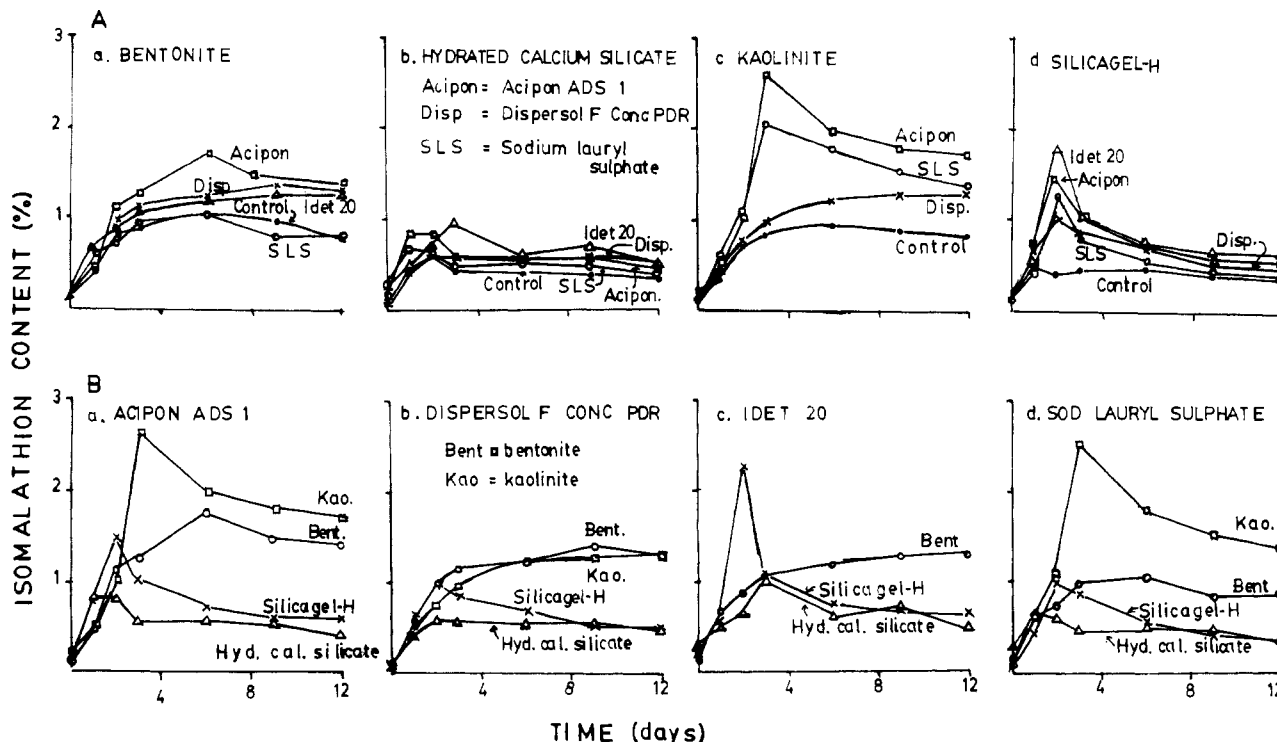


Figure 3. (A) Effect of surfactants on isomalathion content in malathion powders. (B) Relative order among carriers with respect to isomalathion content with different surfactants.

PDR > Idet 20 > sodium lauryl sulfate. Kaolinite: Acipon ADS 1 > sodium lauryl sulfate > Dispersol F Conc. PDR. Hydrated calcium silicate, silica gel H: Idet 20 > Acipon ADS 1 > Dispersol F Conc. PDR > sodium lauryl sulfate.

Isomalathion content of kaolinite-Idet 20 formulation was not estimated since the extraction did not yield clear solution free from suspended clay.

The period of attaining maximum isomalathion content varied with the surfactant and the carrier employed. On bentonite, maximum isomalathion content was observed on the 6th day with Acipon ADS 1 and sodium lauryl sulfate, on the 9th day with Dispersol F Conc. PDR, and on the 12th day with Idet 20. In the case of Kaolinite, Acipon ADS 1 and sodium lauryl sulfate showed maximum isomalathion content on the 3rd day and Dispersol F Conc. PDR on the 12th day. On silica gel H, maximum isomalathion content was on the 2nd day with all surfactants. In the case of hydrated calcium silicate, Acipon ADS 1 and sodium lauryl sulfate showed maximum isomalathion content on the 1st day, Dispersol F Conc. PDR on the 2nd day, and Idet 20 on the 3rd day. Likewise, controls with different carriers too showed maximum isomalathion content on different days. These results once again confirmed the earlier observation by Halder and Parmar (1984) on the periodicity of maximum isomalathion content.

The relative order among surfactants with respect to isomalathion content on different carriers on the day of maxima was as follows. Bentonite: Acipon ADS 1 > Dispersol F Conc. PDR > Idet 20 > control > sodium lauryl sulfate. Kaolinite: Acipon ADS 1 > sodium lauryl sulfate > Dispersol F Conc. PDR > control. Hydrated calcium silicate, silica gel H: Idet 20 > Acipon ADS 1 > sodium lauryl sulfate > Dispersol F. Conc. PDR > control.

For each surfactant the comparative order among different carriers with respect to isomalathion formation is shown in Figure 3B. On the 6th day the order was as follows. Acipon ADS 1, sodium lauryl sulfate: kaolinite > bentonite > silica gel H > hydrated calcium silicate.

Dispersol F Conc. PDR: bentonite > kaolinite > silica gel H > hydrated calcium silicate. Idet 20: bentonite > silica gel H > hydrated calcium silicate.

On the day of maximum isomalathion content the order was as follows. Acipon ADS 1: kaolinite > bentonite > silica gel H > hydrated calcium silicate. Dispersol F Conc. PDR: bentonite > kaolinite > silica gel H > hydrated calcium silicate. Idet 20: silica gel H > bentonite > hydrated calcium silicate. Sodium lauryl sulfate: kaolinite > silica gel H > bentonite > hydrated calcium silicate.

The addition of test surfactants generally resulted in a higher isomalathion content in kaolinite and silica gel H in comparison with their respective controls. Acipon ADS 1 caused high isomalathion content in bentonite and kaolinite and Idet 20 in bentonite and silica gel H. Dispersol F Conc. PDR showed the smallest isomalathion content in silica gel H and hydrated calcium silicate. Sodium lauryl sulfate recorded the smallest isomalathion content in bentonite powders, the values even dipping below control at times.

Effect of Relative Humidity. An increase in the relative humidity (RH) of the storage environment generally increased the isomalathion content (Figure 4). In the case of silica gel H an increase in RH from 41 to 65% increased the isomalathion content but a further increase in RH to 93% only initially increased the isomalathion content and the same decreased with time. In all other cases the isomalathion content was more at higher RH of the storage environment. The same trend was maintained in malathion control.

At a particular RH the different carriers showed the following trend with respect to isomalathion content on the 6th day (Figure 5). 41% RH: Celite > silica gel H > bentonite > Fuller's earth > kaolinite > hydrated calcium silicate > attapulgit. 65% RH: Celite > silica gel H > Fuller's earth > bentonite > kaolinite > hydrated calcium silicate > attapulgit. 93% RH: Celite > Fuller's earth > kaolinite > bentonite > silica gel H > hydrated calcium silicate > attapulgit.

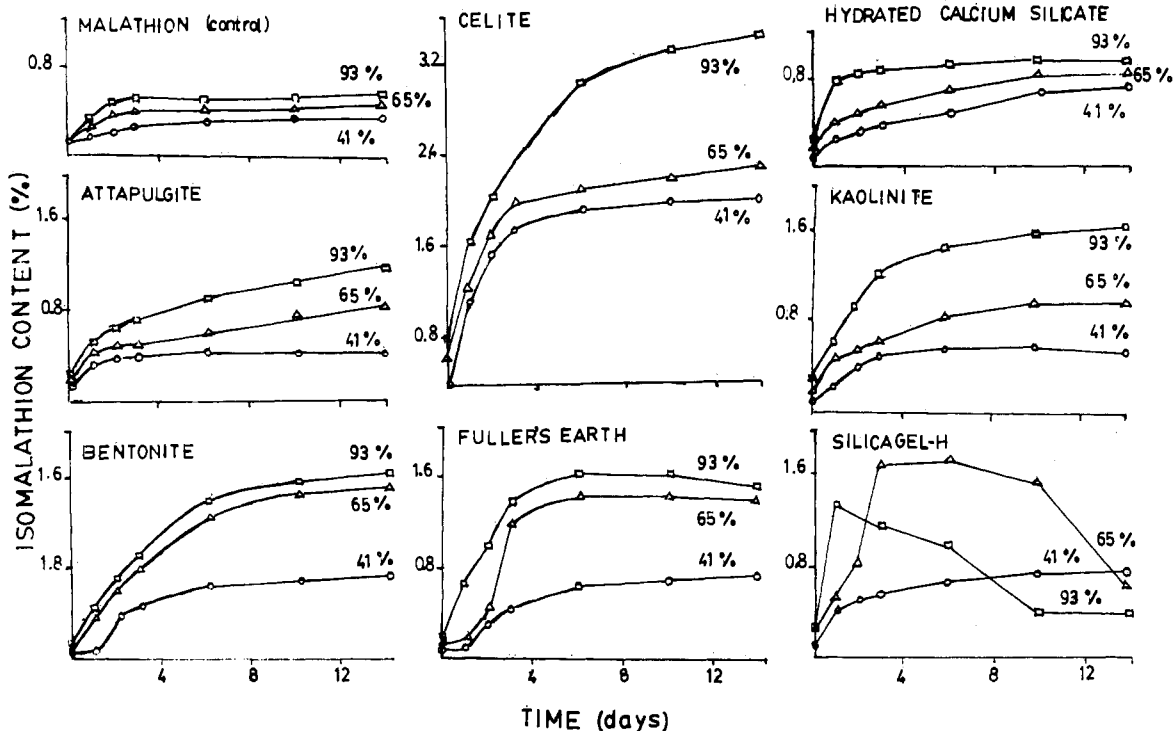


Figure 4. Effect of relative humidity on isomalathion content of malathion powders.

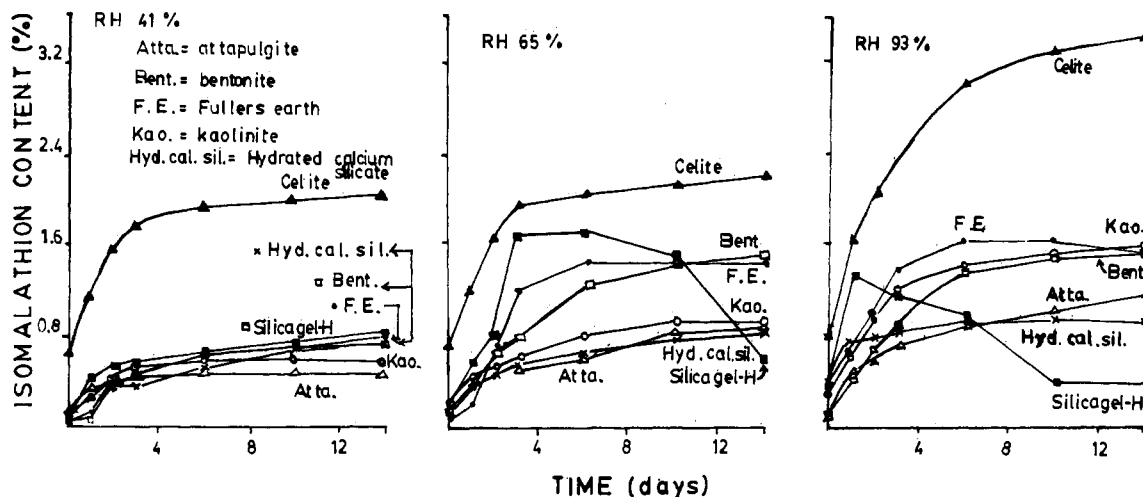


Figure 5. Relative order among carriers with respect to isomalathion content in malathion powders at different relative humidities.

As is apparent, Celite-based malathion formulation was most susceptible and attapulgitte and hydrated calcium silicate were least susceptible to variations in environmental RH.

The period of attaining maximum isomalathion content varied with the carrier and RH. In the cases of attapulgitte, bentonite, Celite, kaolinite, hydrated calcium silicate (except 93% RH, 10th day), and malathion, it was the 14th day. Fuller's earth showed on the 14th day at 41% RH and on the 10th day at other RH values. In silica gel H it was the 14th day at 41%, 6th day at 65%, and 1st day at 93% RH. These observations once again confirmed the observation of Halder and Parmar (1984) on the period of attaining maximum isomalathion content.

Effect of Container Surface. The effect of container surface on isomalathion formation is shown in Figure 6. The three surfaces followed the order glass > aluminum > polyethylene. On the 6th day, the isomalathion content on glass surface was 1.1% of the applied malathion (100 mg on 78.5 cm²) as compared to 0.38 and 0.15% on aluminum and polyethylene surfaces, respectively. It in-

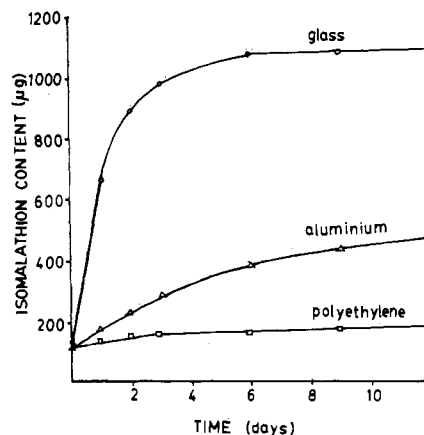


Figure 6. Effect of container surface on isomalathion content of applied malathion films.

creased in all cases with time and was maximum on the 12th day, the respective values on the three surfaces in the

above order being 1.10, 0.48, and 0.19%, respectively. In contrast, the loss of isomalathion (500 μg on 78.5 cm^2) as observed in a related study on these surfaces was only 17.9% on aluminum, 10.4% on glass, and 8.4% on polyethylene during a period of 12 days at 55 ± 1 °C. Thus, over a period of time a net accumulation of isomalathion in such containers was expected. However, the isomalathion content in malathion incubated at 55 ± 1 °C in glass was only 0.33% on the 6th day and ranged between 0.163 and 0.418% during the 14-day incubation period, indicating that the role of container surface in inducing isomalathion formation may probably be confined to the malathion-container interface only.

Effect of Leaf Surface. Isomalathion content of the malathion-treated leaves was not detectable (<0.2 ppm) even when the leaves were treated with a dose 500 times more than the normal application dose. In another study (Rengasamy, 1986) it was observed that nearly 65% of isomalathion applied on leaf surface was lost within 30 min and 99% was lost by the 5th day. A high rate of initial dissipation of isomalathion may account for its non-detection in the present study.

Isomalathion (rat acute oral LD_{50} 113 mg/kg) potentiates the mammalian toxicity of malathion (LD_{50} technical and pure material: 2500 and 12 500, respectively) but not its insecticidal toxicity (Aldridge et al., 1979; Umetsu et al., 1979). The maximum permitted level of isomalathion in malathion water dispersible powders is 1.8% of the nominal malathion content after storage at 55 °C for 6 days (AID/WHO specifications). All concentrations of isomalathion above this level will be lethal.

The present study indicates that various cations that may be present as impurities in carriers or may be added through the formulation auxiliaries, surfactants, and the relative humidity of the formulation environment significantly influence the isomalathion content of malathion powders. The isomalathion content does not increase linearly and its maximum content may exist on any day and not necessarily on the 6th day on storage at 55 °C as implied in AID/WHO specifications. Due caution in the choice of formulation ingredients and its formulation and storage environment is suggested.

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Registry No. Atta, 12174-11-7; Disp, 26545-58-4; Idet 20, 54847-99-3; SLS, 151-21-3; K, 7440-09-7; Ca, 7440-70-2; Na, 7440-23-5; Celite, 12279-49-1; kaolinite, 1318-74-7; silicate, 12627-13-3; acipon, 115305-49-2; aluminum, 7429-90-5; polyethylene, 9002-88-4; isomalathion, 3344-12-5; malathion, 121-75-5.

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