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The mechanism of decomposition of organo-clay complexes is not well established. Allaway[1] believes that at low temperatures the reaction is attended by exothermal changes owing to the combustion of hydrogen released by the cracking of piperidine and at higher temperatures, owing to the combustion of carbon. A stepwise decomposition mechanism for the piperidine-clay complexes suggested by Carthew[2] is based on the volatilisation behaviour of ammonium-

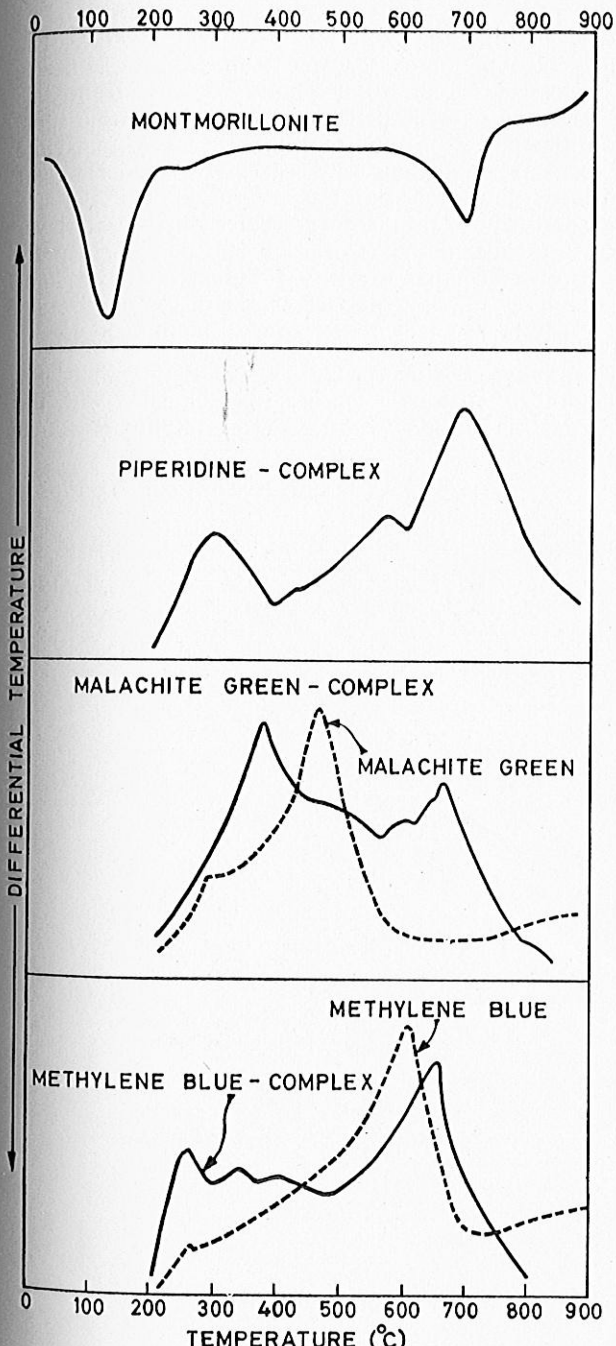

Fig. 1.—*Differential thermal curves of montmorillonite and its complexes.*

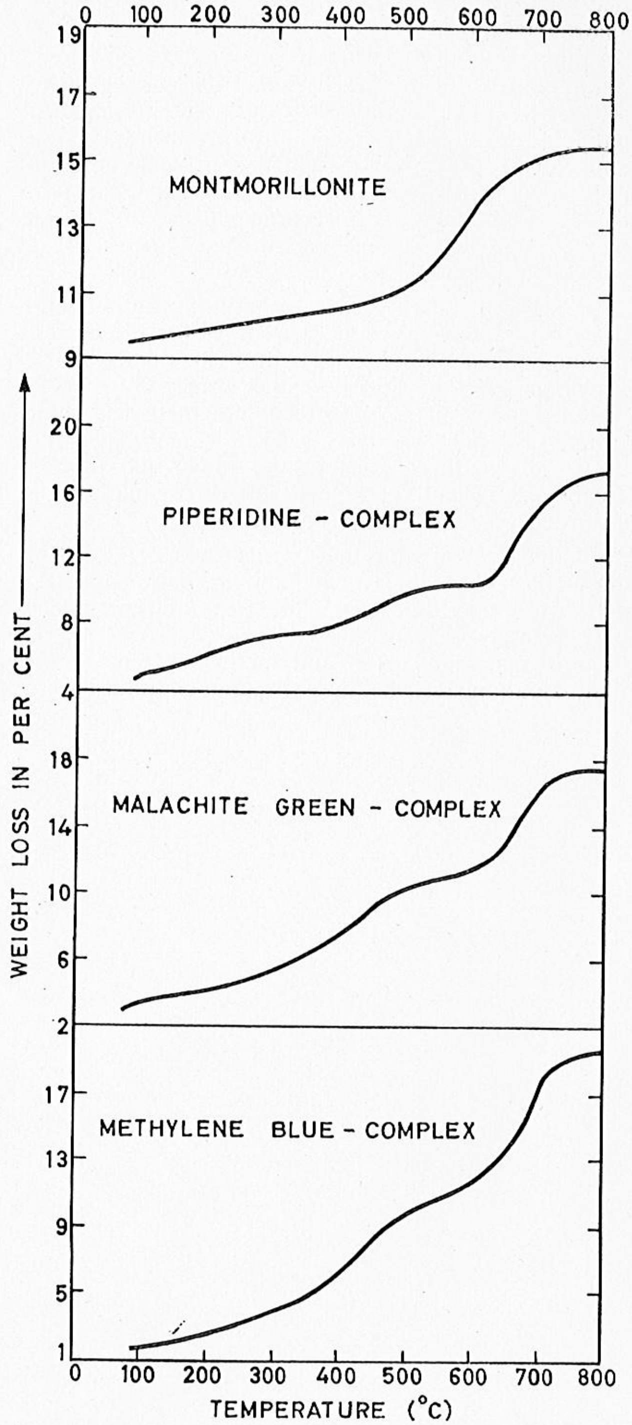

Fig. 2.—*Weight loss curves of montmorillonite and its complexes.*

saturated clay.[3]

We have followed the course of decomposition of three types of organo-montmorillonite complexes by weight loss measurements and have compared the results with thermograms.

A montmorillonite is treated with a known quantity of excess of piperidine, malachite green or methylene blue solution. The unadsorbed organic content is removed by filtration and washing and estimated colorimetrically. By difference, the quantity of organic compound adsorbed on montmorillonite is obtained. Differential Thermal Analysis (D.T.A.) is carried out semi-automatically by raising the temperature of the furnace uniformly using a Leeds and Northrup Programme Controller. The differential temperatures are recorded by a sensitive galvanometer. The weight loss measurements are carried out by heating each sample for three hours at 50°C. intervals up to 800°C.

Fig. 1 gives the D.T.A. of montmorillonite and three complexes. Weight loss curves for the corresponding substances are presented in Fig. 2. The percentage weight losses in the range 150°–400°C. for piperidine, malachite green and methylene blue complexes are respectively 1·53, 3·02 and 3·77 and the corresponding losses in the range 400°–800°C. are 5·72, 6·09 and 11·32 per cent of organic matter adsorbed on the montmorillonite.

Of the total organic matter adsorbed 21·11, 33·15 and 24·98 per cent is decomposed between 150°–400°C. for piperidine, malachite green and methylene blue complexes respectively. The D.T.A. (Fig. 1) of pure malachite green and methylene blue shows that oxidation starts below 200°C. and continues up to 600°–700°C. If cracking of hydrogen is mainly responsible for the exothermic peaks at lower temperatures, the loss of weight should be about 0·6–0·9 per cent of the total weight of the organic compound adsorbed.

The above studies indicate that the organic matter adsorbed on the edges being, easily accessible to oxygen, decomposes exothermally in the range 150°–400°C. Organic matter adsorbed on the interlayer surface is not easily accessible to oxygen and is oxidised after the evolution of the (OH) water. The loss of piperidine at lower temperatures is nearly 20 per cent of the total quantity adsorbed and this corresponds to the percentage of exchangeable spots on the edges of montmorillonite.[4] For malachite green and methylene blue complexes higher weight losses at lower temperatures are caused by a relatively low adsorption of these molecules on the interlayer surfaces due to the "Cover up effect." Incidentally it is observed that weight loss curves of the organo-complexes of clays and clay minerals can advantageously be applied in clay mineral identifications.

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References

[1] Allaway, W. H., *Soil Sci. Soc. Amer. Proc.*, 1948, **13**, 183
[2] Carthew, A. R., *Soil Sci.*, 1955, **80**, 337
[3] Cornet, I., *J. Chem. Phys.*, 1943, **11**, 217
[4] Grim, R. E., "Clay Mineralogy," 1953, *p*. 132. (New York: McGraw Hill Book Co.)

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