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THE EFFECTS OF ADDITIVES ON THE THERMAL DECOMPOSITION OF AZODICARBONAMIDE

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ABSTRACT

The thermal decomposition of azodicarbanamide containing a promotor and pigments is studied by thermal analysis. The promotor used was the "Standere" 3450 containing zinc and cadmium, the activation energies ranged from 25.1 to 38.2 kJ mol^{-1} with different ratios. Six pigments are studied giving a range of activation energy values from 45.3 to 156.8 kJ mol^{-1}.

INTRODUCTION

In an earlier paper [1] results on the thermal decomposition of various commercial samples of Azodicarbonamide (AZ) were reported; most of the results were for pure samples decomposed under various atmospheres, although one or two results were for AZ diluted with alumina. AZ is used extensively in the production of PVC formulations, which may contain substances which are thought to affect the properties of the AZ decomposition; these include

(1) PVC polymer,
(2) plasticizer,
(3) pigments,
(4) promotors (catalysts),
(5) stabilizers,
(6) lubricants.

In this article, we have investigated only two of the above compounds. The effect of promotor and pigments have been studied thermogravimetrically.

Before detailing the new observations, let us recap what is already known about the decomposition of AZ. There is little evidence to suggest that any kinetic studies have been carried out on AZ. However, Reed [2] has investi-

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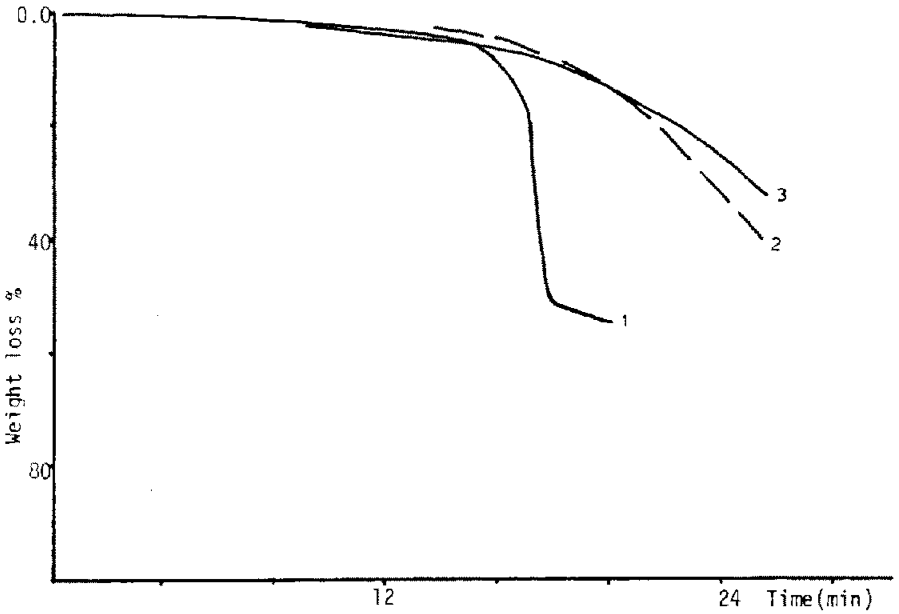

Fig. 1. AZ decomposition, Genitron AC4 dispersed in silicone oil at 193°C. (1) 20% dispersion, (2) 10% dispersion, (3) 5% dispersion.

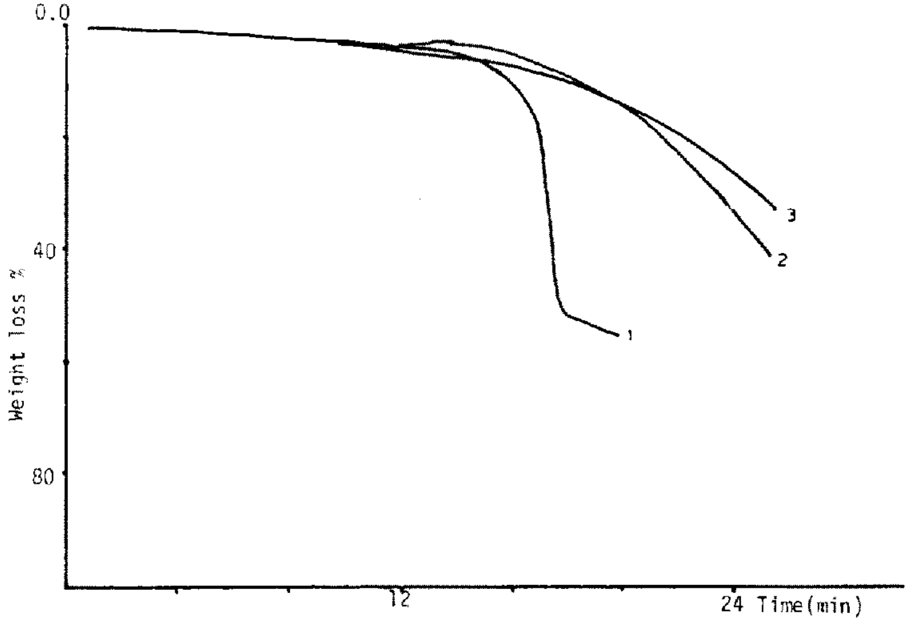

Fig. 2. AZ decomposition, Genitron AC4 dispersed in silicone oil at 202°C. (1) 20% dispersion, (2) 10% dispersion, (3) 5% dispersion.

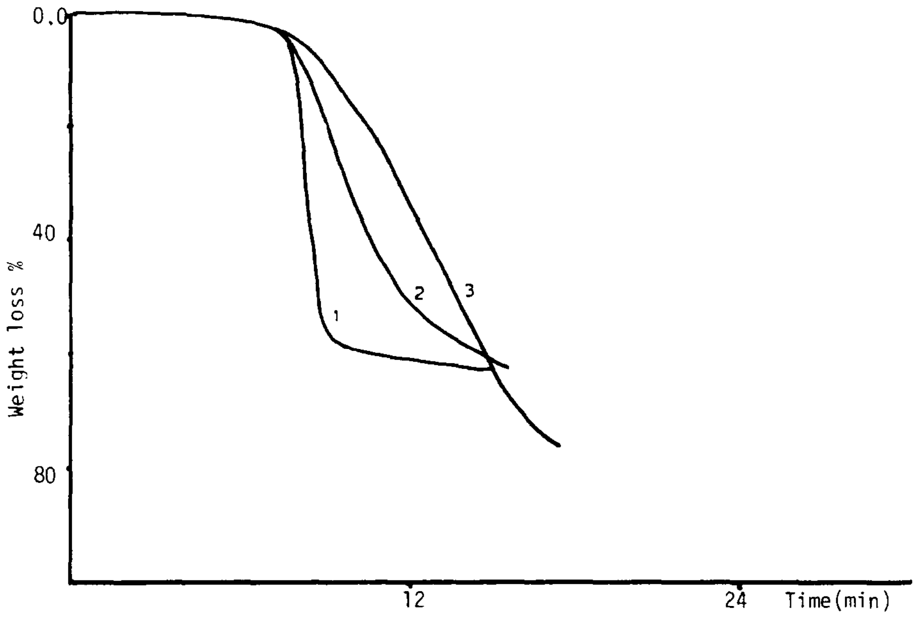

Fig. 3. AZ decomposition, Genitron AC4 dispersed in silicone oil at 213°C. (1) 20% dispersion, (2) 10% dispersion, (3) 5% dispersion.

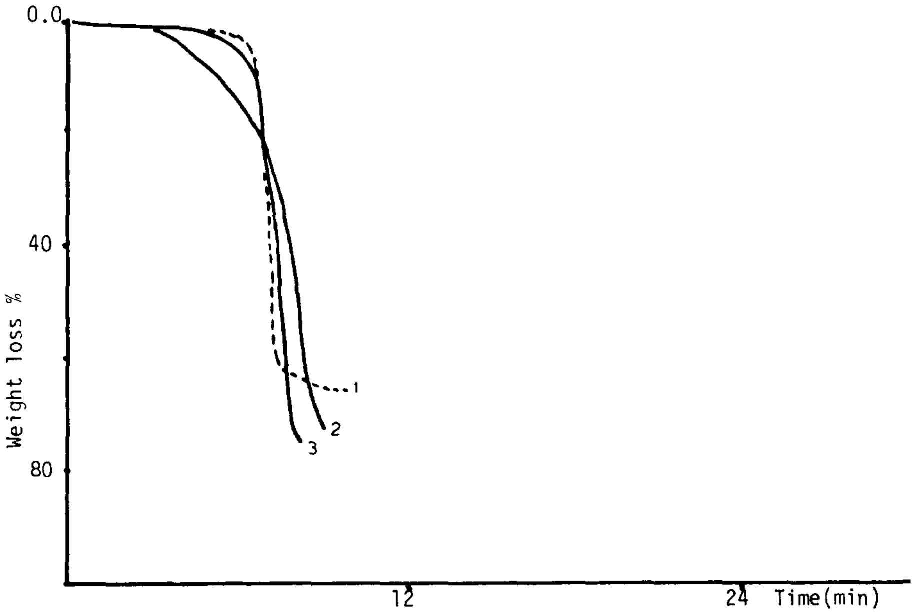

Fig. 4. AZ decomposition, Genitron AC4 dispersed in silicone oil at 225°C. (1) 20% dispersion, (2) 10% dispersion, (3) 5% dispersion.

gated the reaction and it would appear that the primary decomposition follows one of two courses, depending upon reaction conditions

(1) $NH_2CON{=}NCONH_2 \rightarrow N_2 + CO + [NH_2CONH_2 + HNCO + NH_3]$

(2) $2\ NH_2CON{=}NCONH_2 \rightarrow NH_2CONHNHCONH_2 + H_2 + HNCO$

Decomposition of the AZ on heating the dry solid in an open flask at 190°C produces the following (by weight): gases, 32%; solid residue, 41%; sublimate, 27%.

The solid residue comprises: urazol, 39%; biurea, 2%; cyanuric acid, 26%; cyamelide, 1%.

Decomposition at 190°C under the surface of liquid paraffin, however, produces: gases, 34%; residue, 66%.

The residue comprises: urazol, 27%; biurea, 34%; cyanuric acid, 5%.

Thus, the formation of cyamelide and cyanuric acid can be traced from the initial formation of urea or ammonium cyanate, and that of urazol from the intermediate biurea.

EXPERIMENTAL

Equipment and experimental details are given in ref. 1.

RESULTS

Silicone oil was the liquid used in these experiments, being non-volatile and inert under these experimental conditions. Dispersions of Genitron AC4 (20, 10 and 5%) in silicone oil were made up and their properties assessed by thermogravimetric analysis. Decompositions were carried out at constant temperature over the range 190–225°C.

Curves were obtained of varying slopes, an increase in gradient being characteristic of an increase in concentration at constant temperature, or an increase in temperature at constant concentration (Figs. 1–4). By the determination of the gradients of the curves, as in the case of the alumina dilution, activation energies, E_a, were calculated for the different dispersions as follows

% Genitron AC4	20	10	5
E_a (kJ mol^{-1})	122.5	129.4	142.6

As can be seen from these results the values of the activation energies are much higher than those calculated previously. This may be due possibly to a different mechanism or reaction taking place. It can also be seen that a decrease in concentration produces an increase in activation energy (Fig. 5).

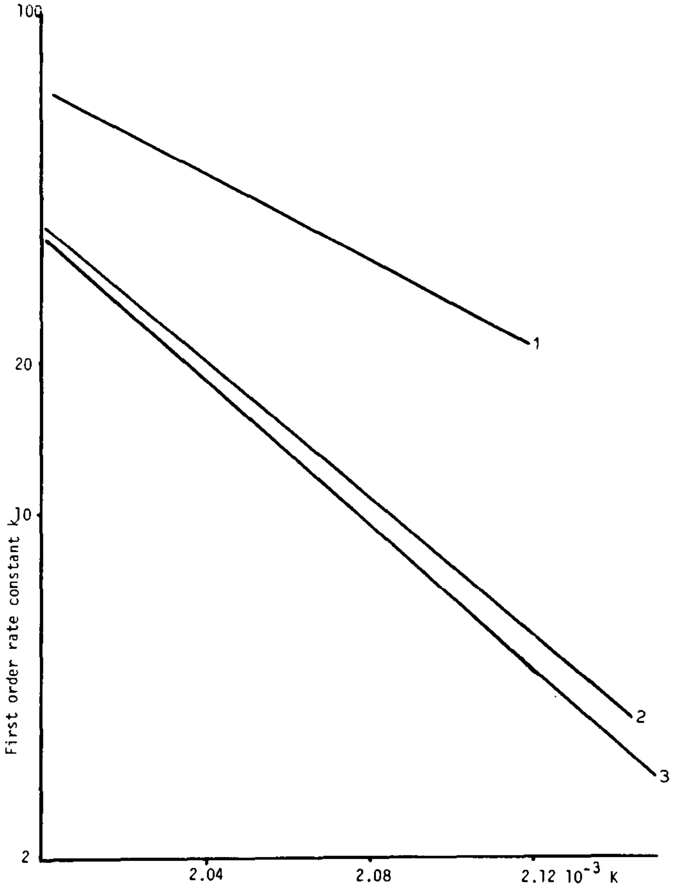

Fig. 5. Arrhenius plots for Genitron AC4 dispersed in silicone oil. (1) 20% dispersion, $E_a = 80.63$ kJ mol^{-1}; (2) 10% dispersion, $E_a = 129.4$ kJ mol^{-1}; (3) 5% dispersion, $E_a = 142.55$ kJ mol^{-1}.

Promotor action

A 2% Genitron AC4 dispersion was mixed with a promotor (S3450) in the ratios 1 : 2, 1 : 1 and 2 : 1.

The promotor used (Stanclere 3450) is known to contain zinc and cadmium but little is known about the cation. It is thought to be a long chain structure of the octoate type. This promotor is supplied as a solution in white spirit.

Decompositions were again carried out isothermally but it was observed that the reaction temperature could be greatly reduced and thermograms were produced over the temperature range 157–225°C (Figs. 6–9). Again curves were produced and similar trends in gradient were observed as with the oil dispersions. Gradients were seen to increase with temperature and

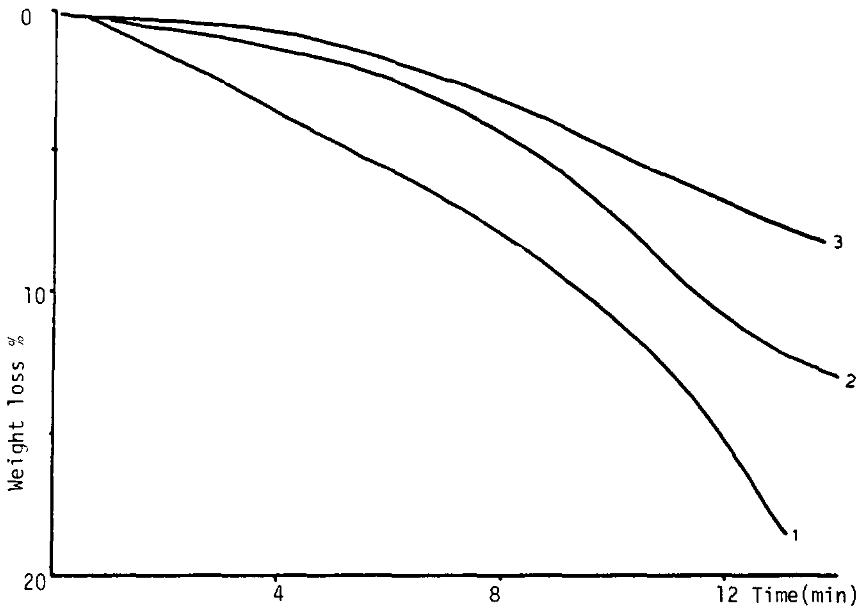

Fig. 6. AZ decomposition, Genitron AC4 with 2% S3450 promotor at 157°C. Genitron AC4: S3450 ratio = (1) 1 : 2, (2) 1 : 1, (3) 2 : 1.

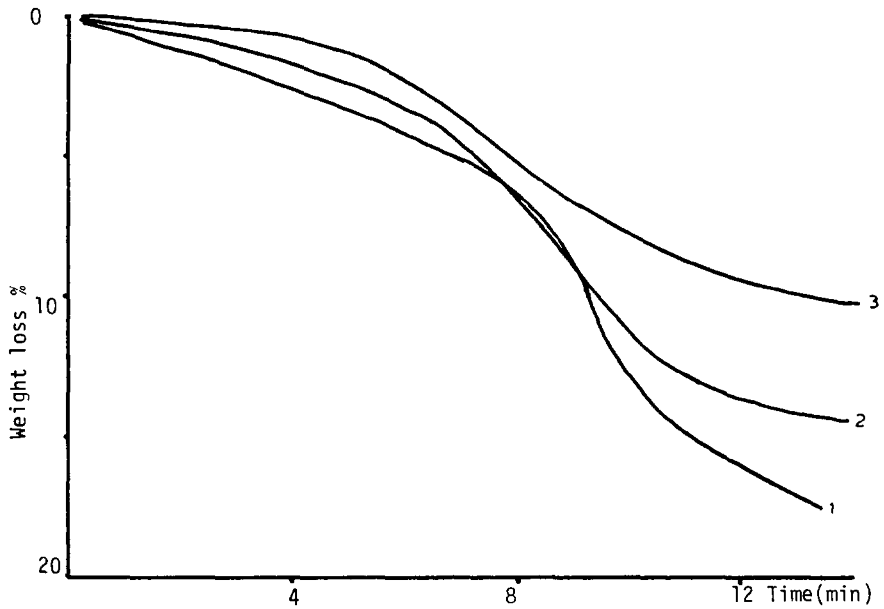

Fig. 7. AZ decomposition, Genitron AC4 with 2% S3450 promotor at 167°C. Genitron AC4: S3450 ratio = (1) 1 : 2, (2) 1 : 1, (3) 2 : 1.

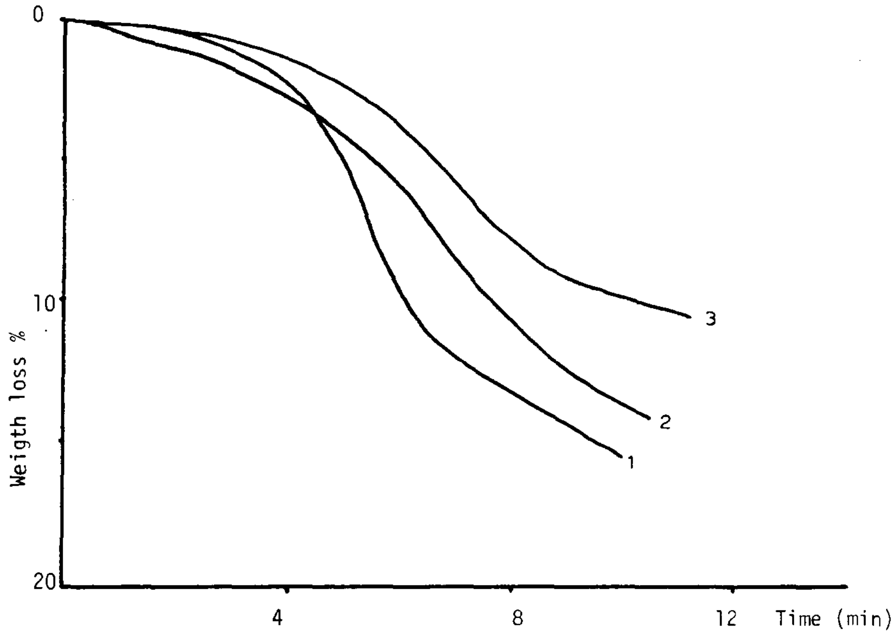

Fig. 8. AZ decomposition, Genitron AC4 with 2% S3450 promotor at 202°C. Genitron AC4: S3450 ratio = (1) 1 : 2, (2) 1 : 1, (3) 2 : 1.

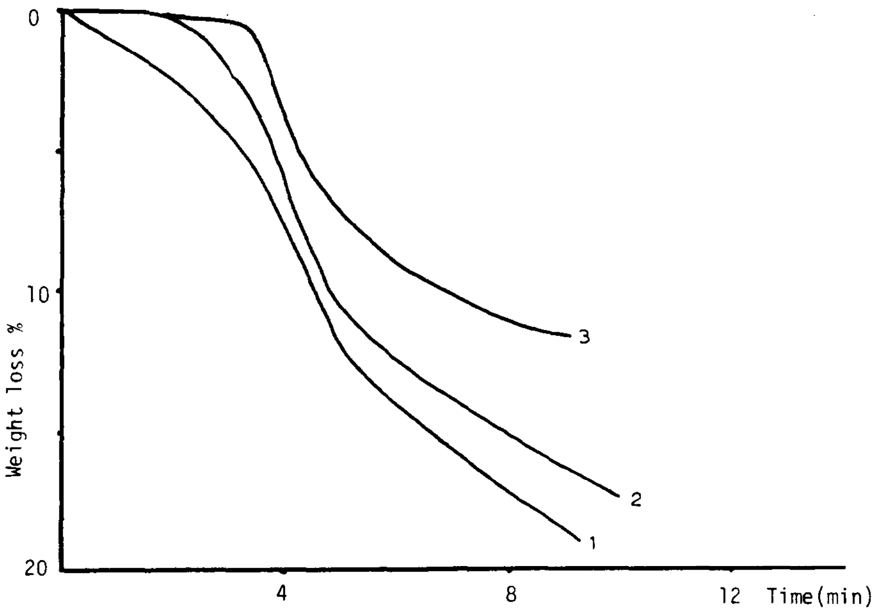

Fig. 9. AZ decomposition, Genitron AC4 with 2% S3450 promotor at 225°C. Genitron AC4: S3450 ratio = (1) 1 : 2, (2) 1 : 1, (3) 2 : 1.

promotor concentration. Activation energy calculations based on Fig. 10 gave the following values

Genitron AC4: S3450 ratio	1 : 2	1 : 1	2 : 1
E_a (kJ mol^{-1})	25.1	38.7	38.2

These values are more indicative of the first type of mechanism or reaction mentioned earlier.

Genitron AC4 was dispersed with the following pigments to produce a 20% dispersion: (i) activated alumina, Al_2O_3 (standard); (ii) mineral black M4730, C; (iii) turkey red oxide, Fe_3O_4; (iv) Rutiox RCR, TiO_2; (v) zinc oxide, ZnO; (vi) cadmium tangerine, CdS/selenite complex.

Isothermal decompositions were carried out over the temperature range 180–225°C (Figs. 11–14). Two types of reaction were observed: (1) The

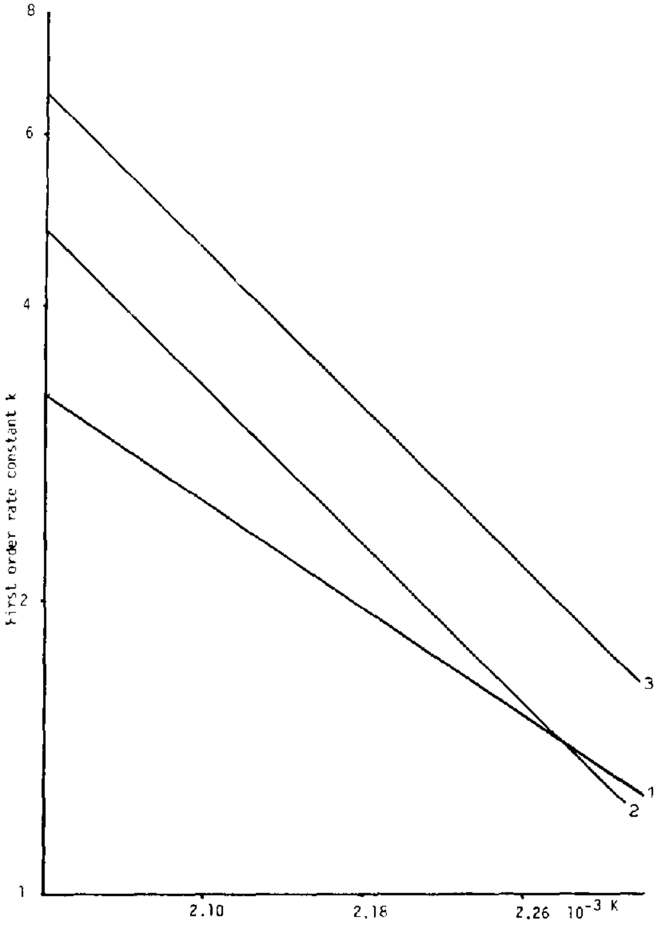

Fig. 10. Arrhenius plots for Genitron AC4 with 2% S3450 promotor. (1) Genitron AC4: S3450 = 1 : 2, E_a = 25 kJ mol^{-1}; (2) Genitron AC4:S3450 = 1 : 1, E_a = 38.6 kJ mol^{-1}; (3) Genitron AC4:S3450 = 2 : 1, E_a = 38.2 kJ mol^{-1}.

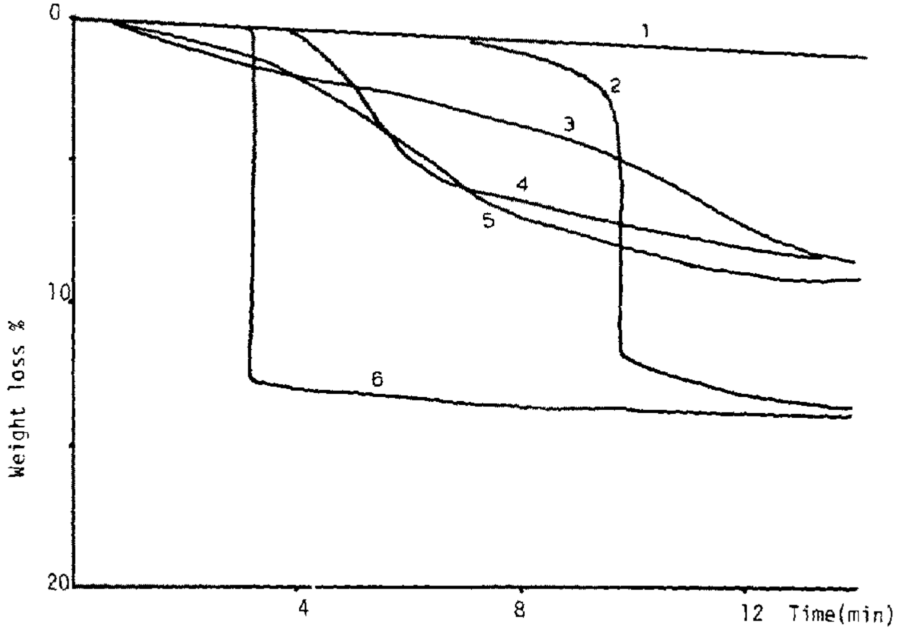

Fig. 11. AZ decomposition, Genitron AC4 with 20% dry pigment at 182°C. (1) Mineral black M4730, (2) turkey red oxide, (3) Rutiox RCR, (4) zinc oxide, (5) activated alumina, (6) cadmium oxide.

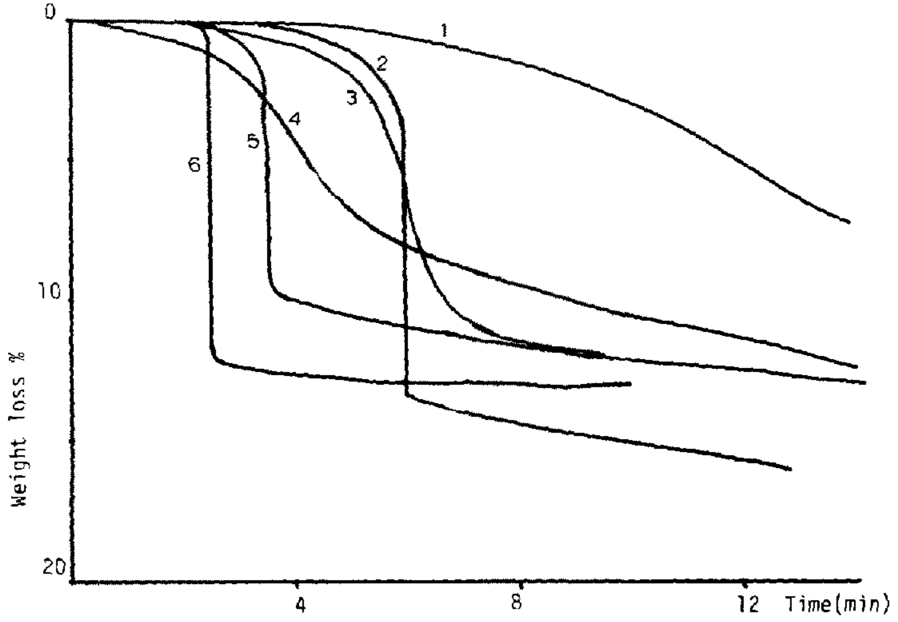

Fig. 12. AZ decomposition, Genitron AC4 with 20% dry pigment at 197°C. (1) Mineral black, (2) turkey red oxide, (3) Rutiox RCR, (4) activated alumina, (5) zinc oxide, (6) cadmium oxide.

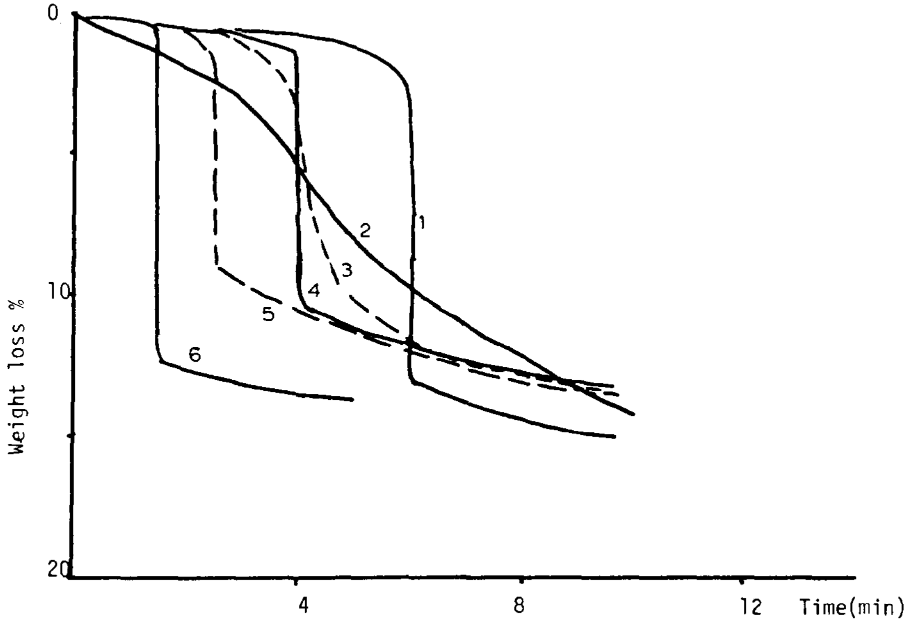

Fig. 13. AZ decomposition, Genitron AC4 with 20% dry pigment at 209°C. (1) Mineral black, (2) activated alumina, (3) Rutiox RCR, (4) turkey red oxide, (5) zinc oxide, (6) cadmium oxide.

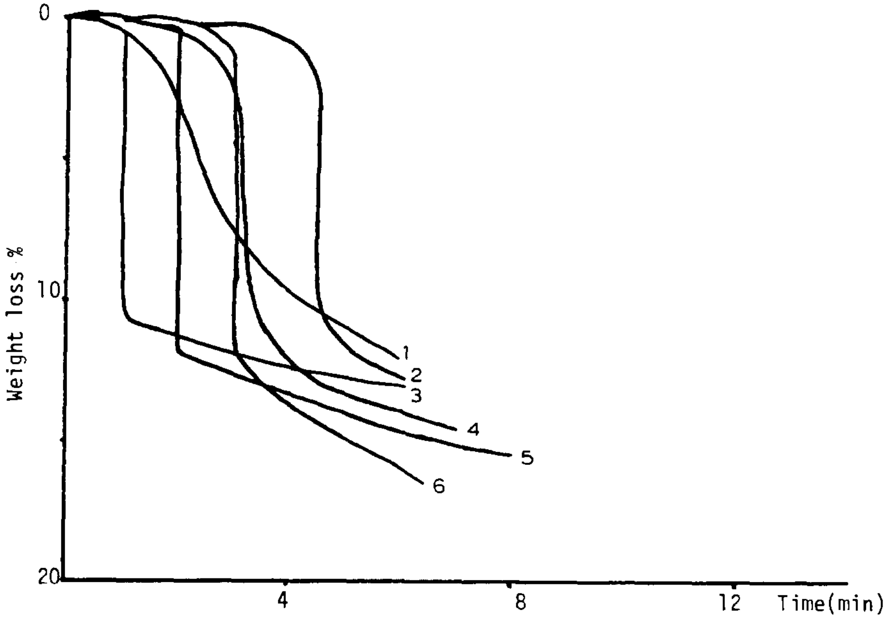

Fig. 14. AZ decomposition, Genitron AC4 with 20% dry pigment at 222°C. (1) Activated alumina, (2) mineral black, (3) cadmium oxide, (4) Rutiox RCR, (5) zinc oxide, (6) turkey red oxide.

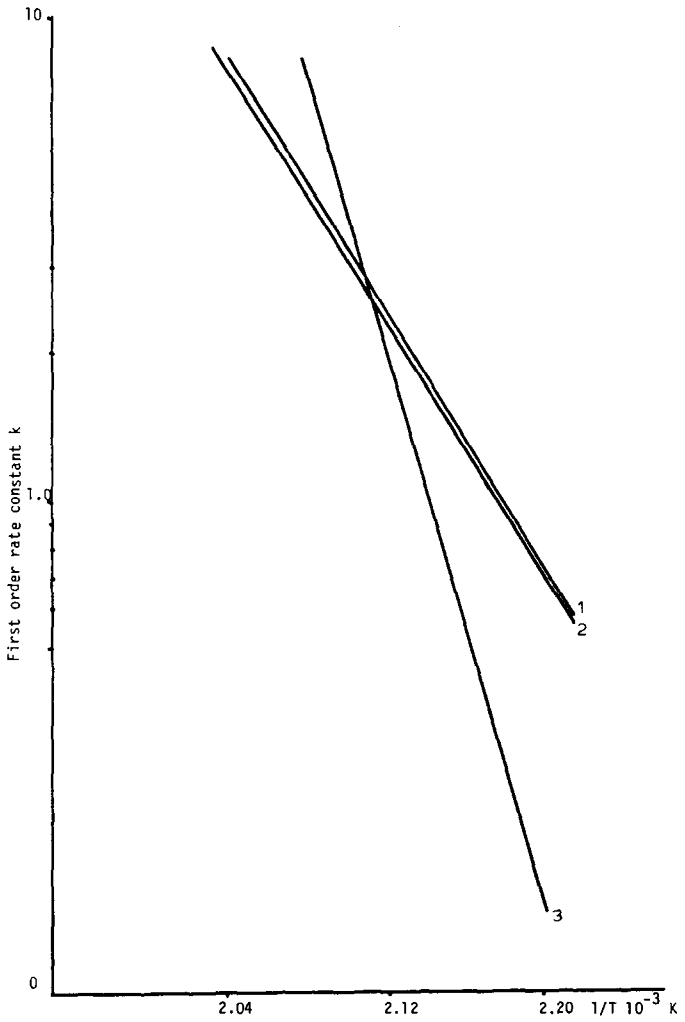

Fig. 15. AZ decomposition, Arrhenius plots for dispersions with 20% dry pigment. (1) Dilution with active alumina $E_a = 124.3$ kJ mol^{-1}; (2) dilution with Rutiox RCR, $E_a = 124.3$ kJ mol^{-1}; (3) dilution with mineral black, $E_a = 156.8$ kJ mol^{-1}.

instantaneous decomposition reaction occurring after a set initiation time; and (2) the gradual decomposition reaction.

Hence, activation energies were determined by the two methods described earlier. The initiation method was found to be applicable to the zinc, iron and cadmium pigments, while the "gradient method" was used for aluminum, titanium and carbon pigments. The following table of activation energies was obtained (Figs. 15 and 16).

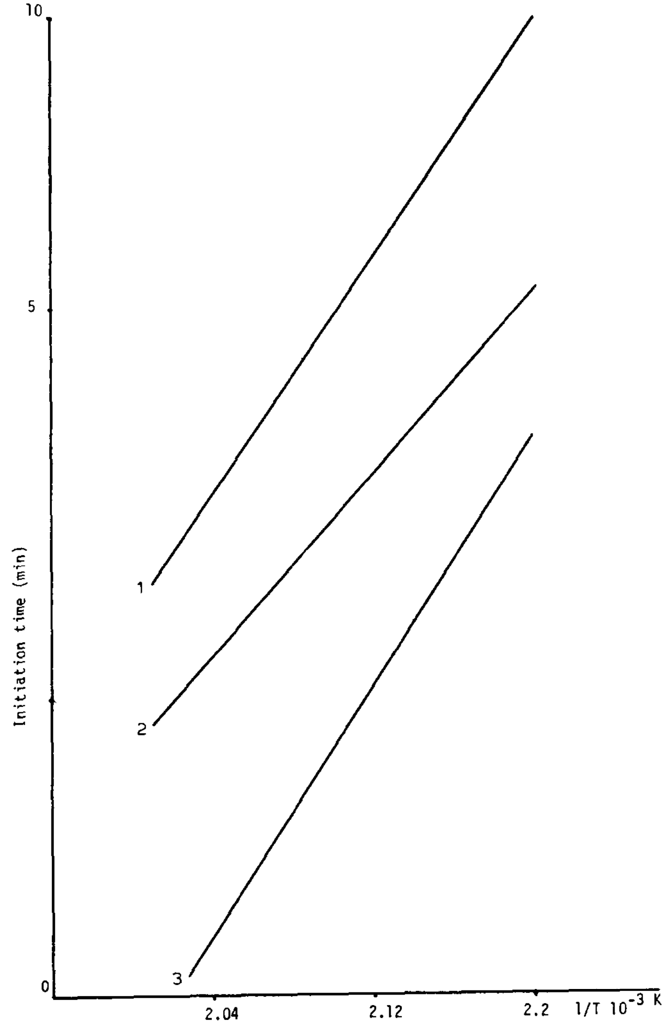

Fig. 16. AZ decomposition, Arrhenius plots for dispersions with 20% dry pigment. (1) Dilution with turkey red, $E_a = 56.3$ kJ mol^{-1}; (2) dilution with cadmium oxide, $E_a = 45.3$ kJ mol^{-1}; (3) dilution with zinc oxide, $E_a = 60.7$ kJ mol^{-1}.

Pigment	E_a (kJ mol^{-1})
Cadmium tangerine	45.3
Turkey red oxide	56.2
Zinc oxide	60.7
Alumina	124.3
Mineral black H4730	156.8

Again, there seems to be the two values of activation energy.

To eliminate any thermal conduction or insulative properties of the

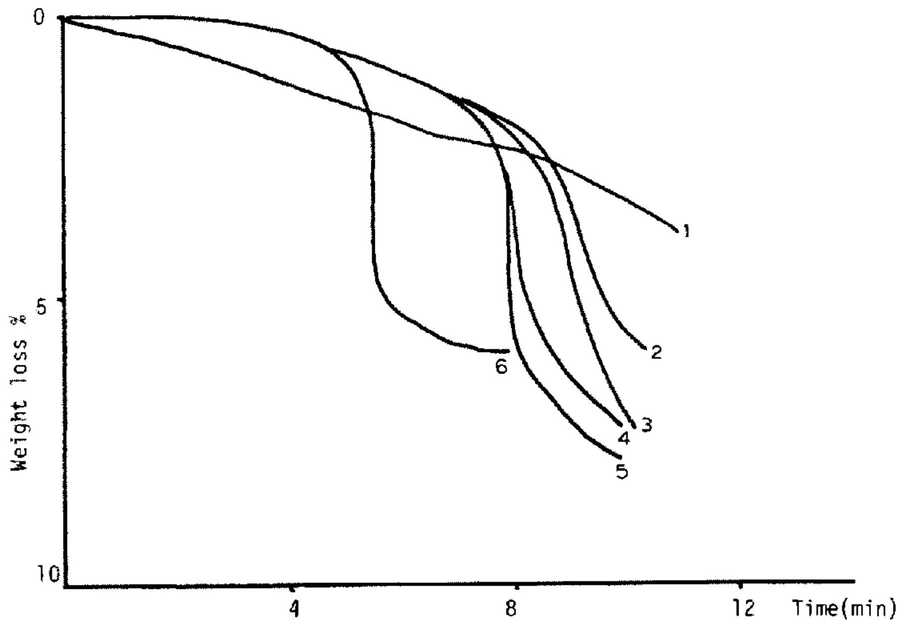

Fig. 17. AZ decomposition, Genitron AC4 with 20% dry pigment dispersed in silicone oil 1 : 1 at 177°C. (1) Activated alumina, (2) mineral black, (3) cadmium oxide, (4) zinc oxide, (5) turkey red oxide, (6) Rutiox RCR.

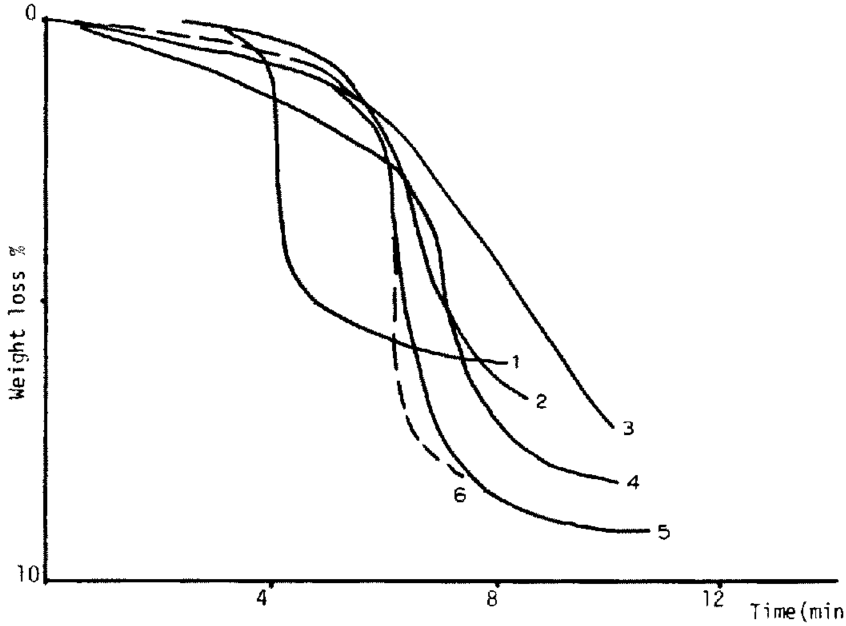

Fig. 18. AZ decomposition, Genitron AC4 with 20% dry pigment dispersed in silicone oil 1 : 1 at 203°C. (1) Rutio RCR, (2) mineral black, (3) activated alumina, (4) cadmium tangerine, (5) turkey red oxide, (6) zinc oxide.

pigments, the dispersions were mixed with silicone oil (1 : 1) and thermograms obtained (Figs. 17 and 18). Similar reactions and curves were obtained.

It can be postulated that the reaction would be favored by the existence of an electron deficient surface to provide easy breakdown of the azodicarbonamide molecule into radicals. This can be found on several pigments and depends upon the promotor used. Three of the pigments were found to be metal compounds of the n-type semiconductors. These compounds are electron deficient systems with either anionic vacancies or interstitial metal ions. The pigments were zinc oxide (ZnO), turkey red oxide (Fe_3O_4) and cadmium tangerine (CdS/selenite complex). Also, the promotor was known to be a zinc/cadmium mixture.

The results, however, indicated two reactions or mechanisms, since two distinct values of activation energy were obtained. Classification of the experiments into these two mechanisms produces the following information

E_a 62–83 kJ mol^{-1}	E_a 125–146 kJ mol^{-1}
Solid, undiluted decompositions	Silicone oil dispersions 20, 10, 5%
Solid, alumina diluted (20%)	
Silicone oil/promotor systems (20%)	Other pigments (10%)
n-Type semiconductor pigments (10%)	

The lower activation energy group (62–83 kJ mol^{-1}) is basically of the explosive type. Dilution with alumina produces a slow reaction but this is simply a dilution effect, the mechanism being the same as in the explosive, undiluted reaction.

The other series of experiments, in which the activation energy was calculated from the measurable rate of the main reaction showed a tendency for the activation energy to be in the region 30–35 kJ mol^{-1}. This occurs when silicone oil is used to disperse the material, and also with 20% dispersions in dry alumina, Rutiox RCR (TiO_2), and mineral black. This indicates that at 20%, the dispersion of the azodicarbonamide is not complete and there must be some aggregation of the particles. It also follows that even at low dispersion values in silicone oil (5%) there is a tendency for the azodicarbonamide to clump together in aggregates. This phenomenon was observed on removing the silicone oil samples after completing a run on the thermogravimetric balance, i.e., the residue had formed in aggregates on the oil surface.

The presence of the promotor in such a system is two-fold. Apart from the catalytic action of the cadmium/zinc compounds there is a contribution from the long organic chain attached to the metal. It is thought to be of the octoate type and hence will act as a "soap", dispersing the individual particles of azodicarbonamide.

REFERENCES

1 A.S. Bhatti and D. Dollimore, Thermochim. Acta, 76 (1984) 63.

2 B. Reed, British Plastics, Oct. 1961, p. 468.