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(Received 10 July, 2002; Revision accepted 28 July, 2003)

**ABSTRACT**

Thermal decomposition studies were carried out on three samples of nickel azide. The samples, prepared using different methods, are fresh nickel azide, fresh nickel hydroxy azide and the third sample was obtained by ageing fresh nickel hydroxy azide for almost one year. Thermal decomposition of the samples at different temperatures was carried out using a locally designed apparatus. The decomposition patterns of each of the samples cannot be explained by a single kinetic law as each of them comprises more than one region or stage of decomposition. Ni(II)N<sub>3</sub> and aged Ni(OH)N<sub>3</sub> decompose with maximum rate from the beginning of the decomposition at all temperatures considered. Ni(OH)N<sub>3</sub> however shows an initial induction period and considerable acceleratory rates before the decay starts. Activation energies calculated from appropriate rate constants gave similar values for the exponential and decay regions for Ni(II)N<sub>3</sub> and aged Ni(OH)N<sub>3</sub> (147± 3 and 74±6KJ mol<sup>-1</sup> respectively) while those for Ni(OH)N<sub>3</sub> in the acceleratory and decay regions are 106KJ mole<sup>-1</sup> for both regions. The overall observation is that ageing of Ni(OH)N<sub>3</sub> brings about the removal of the induction period in the decomposition kinetics similar to fresh Ni(II)N<sub>3</sub>.

**KEY WORDS:** Ageing, activation Energy, Thermal Conductivity, order of Symmetry, Azides

**INTRODUCTION**

The effects of mechanical strain, ageing and additives on the thermal decomposition of inorganic compounds have been investigated in the past (Jacobs and Whitehead, 1969) mainly because of their technological application. For instance ammonium perchlorate is an important rocket propellant. The decomposition of the single crystal of NH<sub>4</sub>ClO<sub>4</sub> is observed to start at the surface but the surprising feature of this reaction is that, in addition to the various gaseous products, a finely divided solid residue is formed, which was analysed and found to be NH<sub>4</sub>ClO<sub>4</sub>. Optical and electronic studies (Herley et al, 1970) on the decomposing crystal show that the decomposition nuclei form more easily where dislocations intersect with the crystal surface. This demonstrates the influence of defect sites on the decomposition of a substance.

The effect of such factors as ageing, pre-irradiation or presence of impurities on the decomposition of inorganic solids is most easily observed in the change in induction periods of their decomposition curve. For instance the induction period for the thermal decomposition of specially purified materials is longer than that for commercially available ones which may contain some impurities.

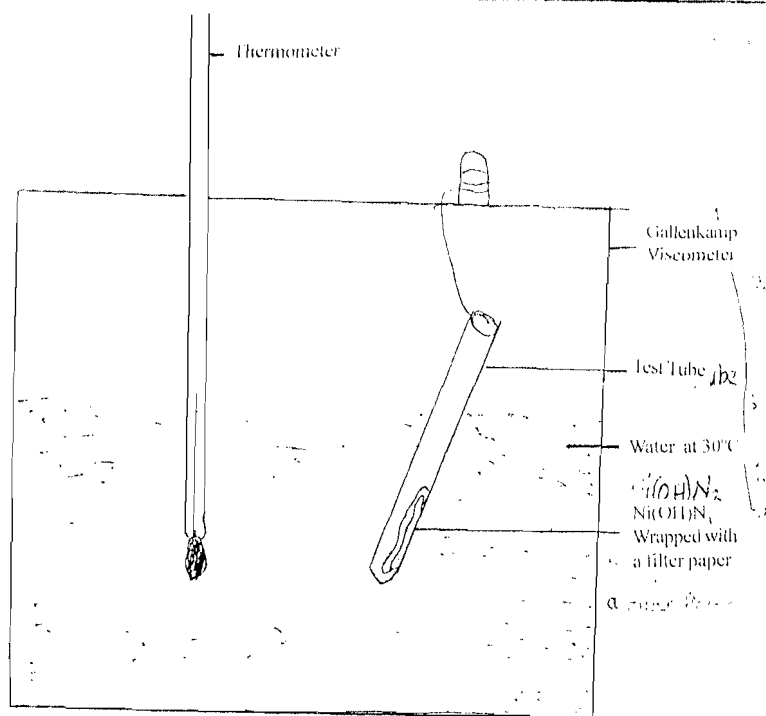
Inorganic solid azides are technologically important in medicine, military and mining fields, among other areas. Azides such as the transition metal azides and their complexes can be extremely explosive upon the application of

impact, shock or friction. Ni(N<sub>3</sub>)<sub>2</sub> has been reported to be a very sensitive explosive (Wohler and Martins, 1917).

Sood and Nya (1981) have reported on the thermal decomposition of Ni(N<sub>3</sub>)<sub>2</sub> although the effect of any contamination on the decomposition of the sample was not studied. The present investigation explores the alteration of decomposition rates of different samples of nickel azides caused by; (1) ageing and (2) substitution of an N<sub>3</sub><sup>-</sup> with an OH<sup>-</sup> group which, in most preparations of Ni(N<sub>3</sub>)<sub>2</sub>, form contaminants on the azide. The activation energies, E<sub>a</sub>, of decomposition of each of the samples are calculated theoretically from the rate constants obtained from their thermal decomposition in order to determine the degree of stability of the samples. Having determined E<sub>a</sub> for each sample it is then possible to ascertain its explosivity at room temperature using recommended techniques eg, by weight drop or applied potential (Sood and Alobi, 1996). If it is found to detonate on application, for example of electrical field, it can be employed in mining and other exploration fields and can therefore be recommended as a cheap detonator for use in various mining operations currently taking place in Nigeria.

**MATERIALS AND METHODS**

Thermal decomposition of nickel azide has already been studied (Sood and Nya, 1982). Contamination of the normal nickel azide, Ni(N<sub>3</sub>)<sub>2</sub>, (during evaporation) by a layer of basic

FIG. 1: AGEING OF Ni(OH)N<sub>3</sub>

nickel azide has however necessitated a more careful study of the thermal decomposition of the azide. The samples used for the thermal decomposition are:

- (i) Fresh nickel azide [Ni(N<sub>3</sub>)<sub>2</sub>], referred to as sample 1.
- (ii) Fresh nickel hydroxy azide [Ni(OH)N<sub>3</sub>] designated as sample 2 and
- (iii) Ni(OH)N<sub>3</sub>, ground and aged for 360 days in vacuum over P<sub>2</sub>O<sub>5</sub>, called sample 3.

(i) Fresh anhydrous nickel azide, (sample 1) was prepared by distilling HN<sub>3</sub> over NiCO<sub>3</sub> followed by filtration and crystallization. The crystals were ground very mildly in a dehumidified atmosphere (relative humidity < 60%) and stored in vacuum over P<sub>2</sub>O<sub>5</sub> for 30 days before the kinetic studies were performed. The sample, determined volumetrically with EDTA and Van der Moulén methods (1961), has a composition of Ni(N<sub>3</sub>)<sub>2</sub>. Vander Moulén method involves the reaction of the azide with excess of KMnO<sub>4</sub> in acid solution and back titrating with KI in order to estimate the amount of KMnO<sub>4</sub> that liberates all the nitrogen from the azide using sodium thiosulphate.

(ii) A fresh sample of Ni(OH)N<sub>3</sub> was prepared by first dehydrating nickel azide dihydrate, Ni(N<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, crystals over P<sub>2</sub>O<sub>5</sub> and then exposing the normal nickel azide to moist atmosphere (R.H > 80%) for several days.

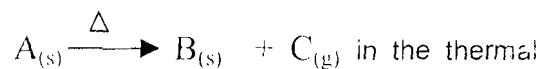
The sample was thereafter mildly ground and stored in a vacuum of 1.33 × 10<sup>-3</sup> mbars over P<sub>2</sub>O<sub>5</sub> for 30 days. It was not subjected to further grinding during the decomposition studies. The composition was established by titrimetric method to be Ni(OH)N<sub>3</sub>.

- (iii) A fresh sample of Ni(OH)N<sub>3</sub> was again mildly ground and aged for 360 days in a vacuum of 1.33 × 10<sup>-3</sup> mbars over P<sub>2</sub>O<sub>5</sub>. Ageing of sample 2 was done in a viscometer bath with water at 30°C circulating constantly throughout the period of ageing (figure 1). A mechanical stirrer was used to ensure uniform temperature of the sample at any instant time. The sample was ground very mildly before the decomposition studies were carried out.

Isothermal decomposition studies for the three samples were carried out within a temperature range of 480°K to 548°K. the decomposition in each case was carried out using a vacuum system evacuated to a pressure of 10<sup>-6</sup> mbars

(figure 2). The total volume of the system is 2.9581.

The vacuum system is designed such that the progress of a typical reaction of the form,



in the thermal decomposition unit, F, can be monitored by measuring the pressure of gas, C, produced as a

function of time at different temperatures. In the case of azide decomposition, conditions of very low pressures (e.g,  $10^{-6}$ mbar) are employed so that minimal amounts of samples are used because most inorganic azides are explosive. A combination of both diffusion and rotor pumps is employed in the system to evacuate it down to a pressure of  $10^{-6}$ mbar when required.

In every run 2mg of each of the samples was accurately weighed into the sample-bucket, B. This was suspended from a winch by means of a copper wire and kept in the upper portion of the decomposition tube far enough from the heating zone, F. The sample was then evacuated for 24 hours. Meanwhile the decomposition tube was maintained at the desired temperature for several hours after which the bucket was lowered to the bottom of the decomposition cell (covered by the furnace, F). The process was accompanied by a fall in temperature of about  $1^{\circ}\text{C}$  and the system took 5-10 minutes to adjust to the original temperature. The pressure of nitrogen produced was measured with the help of McLeod Guage (MG) as a function of time. The pressure values were corrected for the initial degassing rate.

The control of the temperature of decomposition was a very important factor during the decomposition measurements. It was found that the temperature of the sample increased slightly with the progress of decomposition even

though the initial temperature was set constant when the system was under vacuum. This behaviour is due to the increased conductivity of the walls of the decomposition tube in the course of reaction. It was therefore necessary to keep a constant watch over each kinetic run. The temperature of the reaction vessel was therefore maintained at constant value within  $\pm 0.25^{\circ}\text{C}$  by an electronically controlled furnace.

RESULTS

The primary kinetics for the thermal decomposition of sample 1 in the temperature range of 480K to 548K are presented in figure 3.

At all temperatures covered, the sample decomposes with maximum rate at the beginning of decomposition. The rate progressively decreases with increasing degree of decomposition which is in agreement with the results of Sood and Nya (1982) who reported that the decomposition rate is maximum at the onset of the decomposition. The maximum value of the degree of decomposition, ' $\alpha$ ' that could be recorded was 0.71, above which the sample exploded.

The kinetic data for the entire decomposition could not fit into a single rate equation in the temperature range considered. The initial portion could best be described by an exponential law (fig 4b) for which the Erofeev equation could be solved to obtain,  $\alpha = 1 - \exp(-$

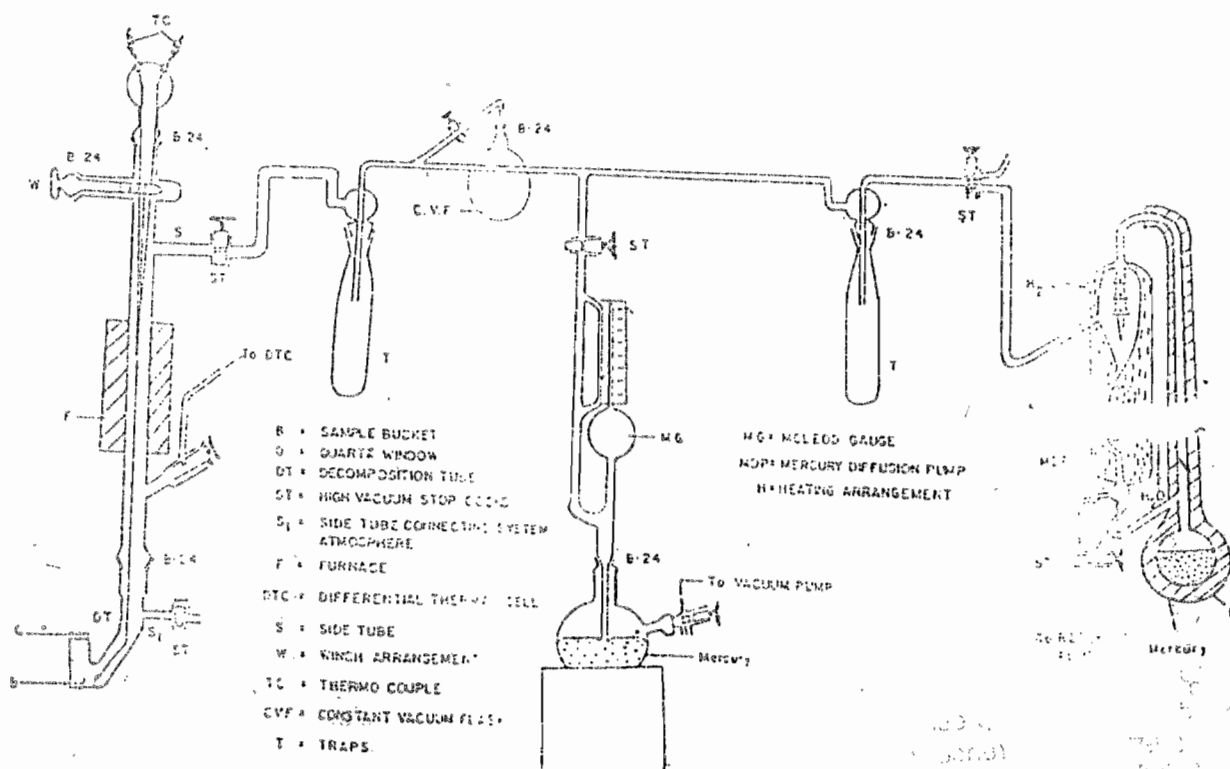


FIG. 2: MAIN VACUUM LINE

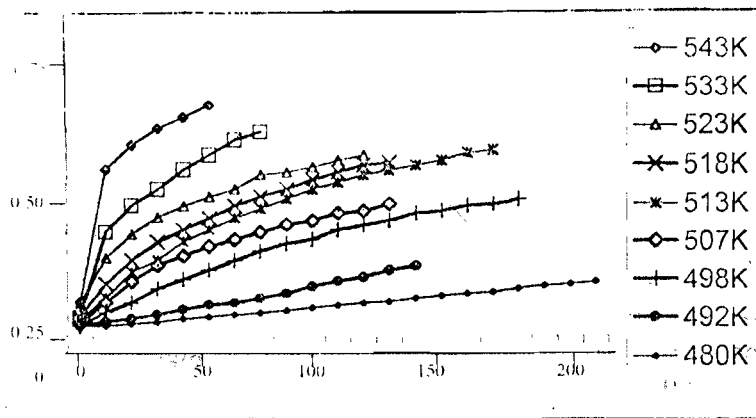


FIG. 3: Thermal decomposition of nickel azide, sample 1, at different temperatures ( $\alpha = P_t/P_z$ ,  $P_t$  = Pressure developed at any time,  $t$  and  $P_z$  = Pressure developed at complete decomposition)

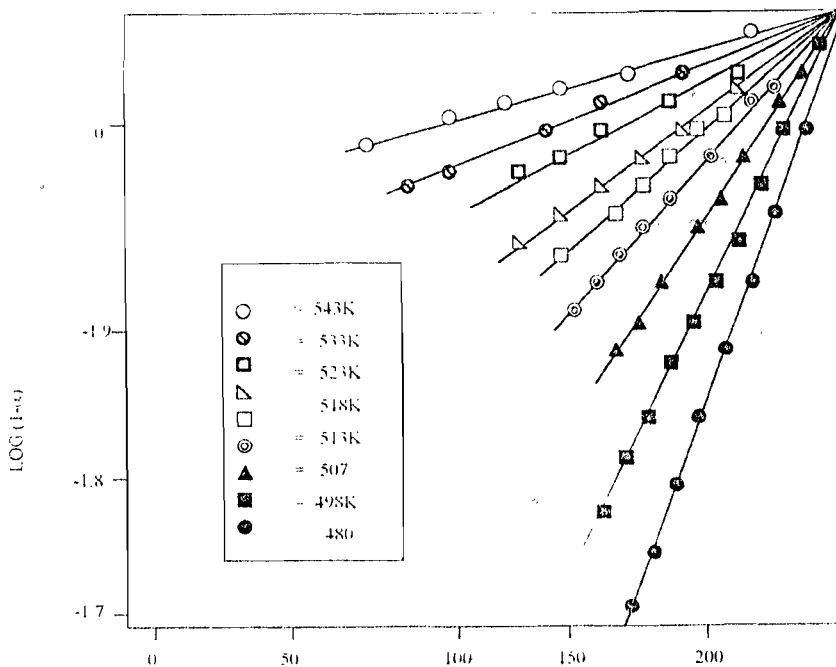


FIG. 4 Plot of  $\text{Log}(1-\alpha)$  vs  $t$  FOR NICKEL AZIDE, SAMPLE 1

kt) (Jacobs and Tompkins, 1955) while the later stages of the decomposition fit into a contracting volume kinetics presented in fig. 5 (Young, 1966).

The energies of activation for both regions are calculated from a plot of log of the rate constants of the exponential/decay reaction at different temperatures versus  $1/T$ . The values of  $147.15\text{KJ mole}^{-1}$  and  $82.0 \pm 3\text{KJ mole}^{-1}$  were obtained for the exponential and contracting volume regions respectively.

The kinetic data for the thermal decomposition of sample 2 within the same temperature range are presented in figure 6. The most significant difference from the curves in

figure 3 above is the sigmoidal character of the curves in figure 6.

The initial stages of decomposition show considerable acceleration before the decay starts. The data for acceleratory region fitted into a plot of  $-\log(1-\alpha)^{1/4}$  VS  $t$ , which is the Avrami-Erofeev equation given in figure 7 with an exponent of '4' up to the inflexion point. The deceleratory region (decay region) could be described by a contracting volume law (fig 8) as in sample 1. The corresponding activation energies obtained from arrhenius plots are  $106.2\text{KJ mole}^{-1}$  for both regions. This is quite a surprising feature about the thermal decomposition of sample 2.

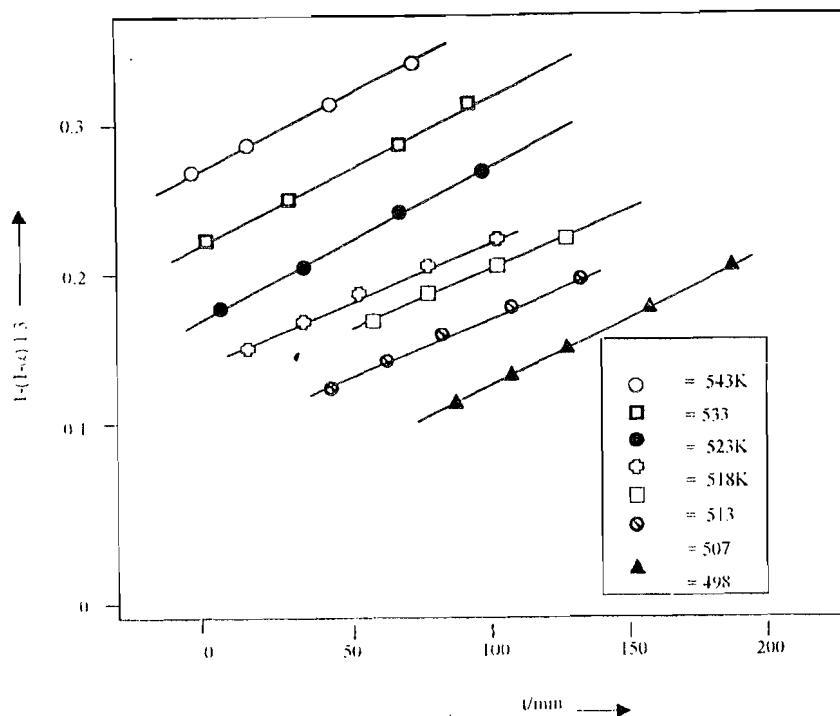


Fig. 5: PLOT OF  $1-(1-\alpha)^{1/3}$  VS T FOR NICKEL AZIDE, SAMPLE 1

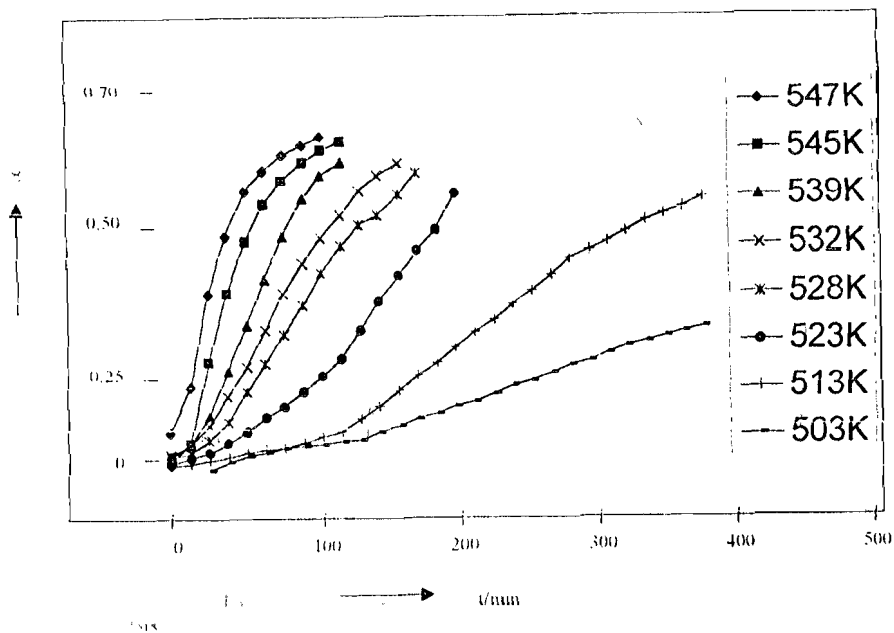
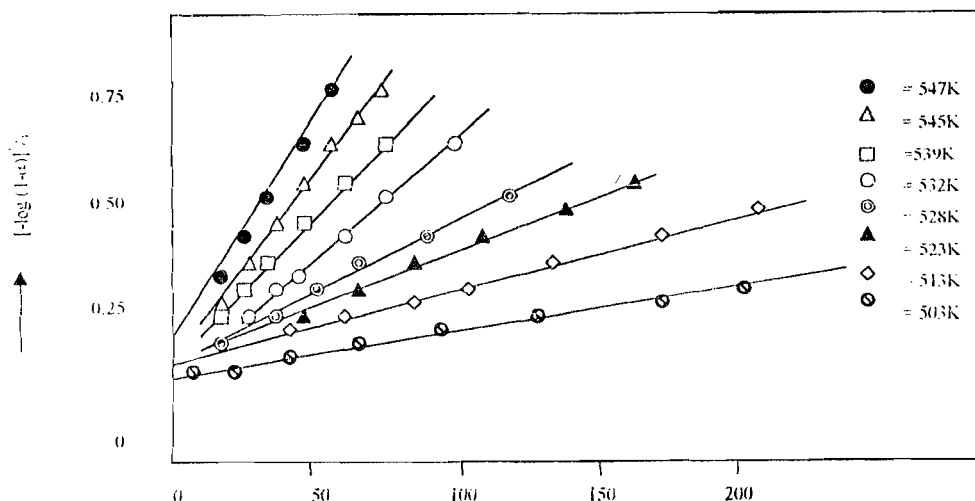
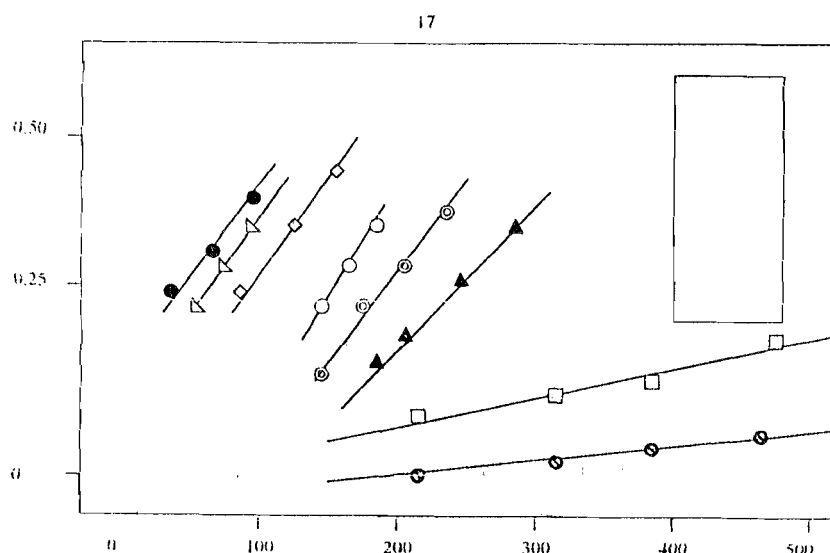


Fig. 6: THERMAL DECOMPOSITION OF sample 2 (fresh but aged for 1 month)

The kinetics for sample 3 were deceleratory throughout its decomposition within the same temperature range as in the case of sample 1 (fig 9). Such could be described by a unimolecular decay law in the initial stages and then a contracting cube equation during the final stages of decomposition. The energies of activation corresponding to the two regions of decomposition are  $150.02 \pm 6$  and  $74.94 \pm 4$  kJ mole<sup>-1</sup> respectively. The results of thermal decomposition of the three samples of nickel

azide as presented in the figures lead to the following considerations:-

- (a) The rate of decomposition at constant temperature decreases with age of the sample. However, on grinding the aged sample as in the case of sample 3, the rate of subsequent decomposition increases slightly. Thus the times required for 40% decomposition at 515°k for samples 2 and 3 are shown in the graph to be 280 and 155 minutes

Fig. 7: PLOT OF  $[-\text{Log}(1-\alpha)]^{1/2}$  Vs t FOR SAMPLE 2FIG. 8: PLOT OF  $1-(1-\alpha)^{1/2}$  Vs t FOR SAMPLE 2.

- respectively.
- (b) The energies of activation for the exponential region in samples 1 and 3 remain virtually constant ( $150 \pm 6 \text{KJ mol}^{-1}$ ) while the Avrami-Erofeev region in sample 2 has a lower value of activation energy ( $106.2 \text{KJ mole}^{-1}$ ). Sample 2, however, has a higher value of  $E_a$  ( $106.2 \text{KJ mole}^{-1}$ ). Sample 2, however, has a higher value of  $E_a$  ( $106.2 \text{KJ mole}^{-1}$ ) in the contracting volume region.

## DISCUSSION

The  $\alpha$ -t curves for exothermic decomposition are generally sigmodal in shape. The shape of the  $\alpha$ -t plots for the isothermal

decomposition of fresh nickel azide and aged nickel hydroxy azide is somewhat unusual although similar deceleratory kinetics have been reported for lead chlorate (Solymosi and Bansagi, 1968), finely powdered silver azide (Bartlet, et al, 1958) and sodium bromate (Young, 1966). The initial deceleratory stage can be described only by an exponential decay law in the case of decomposition of nickel azide (Sood and Nya, 1981). In order to determine the appropriate law to describe the experimental results of the decomposition we need to make reference to  $\alpha$ -t plots of the aged sample presented in figure 9.

Ageing brings about changes in the physical structure of freshly prepared materials which determines, to varying degree, the kinetics

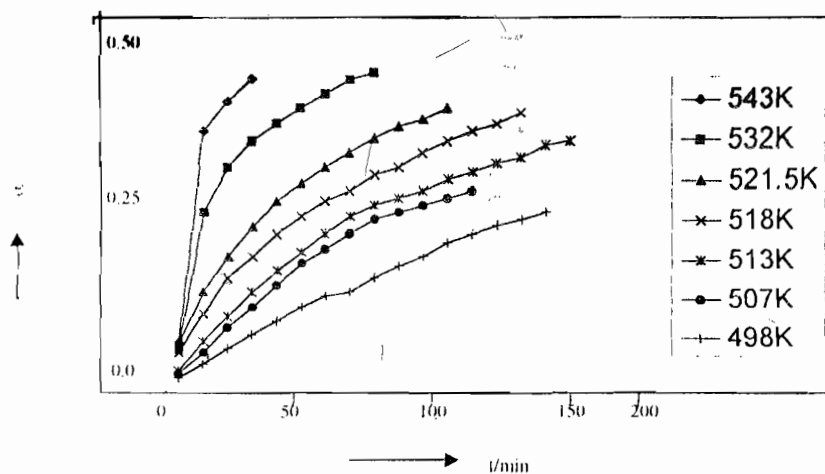


Fig. 9. THERMAL DECOMPOSITION OF sample 3 (aged one year)

of its decomposition. For instance much of irreproducibility of kinetics of isothermal decomposition of freshly prepared barium azide (Jacobs and Tompkins, 1955, Erofeev and Sviridov, 1958), silver oxalate (Finch, et al, 1954), mercury fulminate (Bartlett, et al, 1956) and potassium permanganate (Erofeev, 1961) has been explained on the basis of ageing effects. The freshly prepared mercury fulminate, for example, decomposes according to exponential law whereas a cubic law is found to hold for well-aged samples of the compound (Bartlett et al.,

1957). The exponent of power law in the decomposition of fresh barium azide is 6 and falls to 3 after ageing at room temperature for several months. The sites which were thermally transformed to germ nuclei are removed by annealing during ageing and decomposition is thus desensitized. The desensitization effect of ageing was further confirmed by Yoganarasimhan and Tompkins (1967) while working on barium azide.

Sood et. al. (1982) also made systematic studies on the ageing of zinc azide by following the decomposition for the first 31 days after preparation and concluded that the rate falls for the first 20 days and then attains a constant value. They did not notice any significant change in the kinetics form, may be, because the sample was not aged sufficiently long. It is in view of this unanswered possibility that the present investigation on the decomposition of aged nickel hydroxy azide (aged for 360 days) has been carried out.

The rate of decomposition of sample 3 increases as compared to that of sample 2 even though it is obtained from sample 2 by ageing. Figures 3 and 9 show the enhanced rate of decomposition of fresh normal nickel azide and aged nickel hydroxy azide. In contrast to the

aged sample (sample 3) where nucleation is instantaneous or at least rapid, the appearance of a short induction period followed by acceleration in the decomposition profile of sample 2 (fig 6) points towards time-dependent nucleation. Also the applicability of the Avrami-Erofeev equation (Erofeev, 1991),

$$-\log [(1-\alpha)^{1/n}] = Kt, n = 4$$

to the decomposition data of this sample suggests that the reaction is a single-step random nucleation, i.e.  $dN/dt \approx K_n N_0 t^{n-1}$  (where  $n = 4$ ) with a three-dimensional growth of the nuclei. The model of nucleation to be applied to samples 1 and 3 is the exponential law of nucleation.

The kinetic forms used in the determination of the mechanism studies of the decomposition reactions of solids are based upon quantitative consideration of the nucleation and growth of particles of the product (Bagdassarian, 1945; Jacobs and Tompkins, 1955). Conformity of the kinetic forms to the appropriate theoretical equation indicates, but does not necessarily prove, the occurrences of a particular reaction mechanism. The actual form of the nucleation law and the geometry of the reactant-product interface which are the basis of establishing the mechanism of reaction are, however, very difficult to define without making direct microscopic observations (Garner, 1955). Wischin, (1939) for instance, was one of the earliest scientists to make simultaneous pressure-time measurements and careful examination of the crystal of barium azide under a microscope at different stages of decomposition. It was observed that the nuclei increase in number as the third power of time and grow linearly in radius with time. It has also been reported (Walker, 1969) that the scanning electron micrography of thallos azide shows that the decomposition advanced predominantly in the

(110) direction and bored holes of constant cross section.

The variation in the rate of sigmoidal mode of decomposition of solids is generally ascribed to three factors namely;

- (i) Autocatalytic effect of the solid product (Jacobs, and Tompkins, 1955, Young, 1966).
- (ii) Partial melting as a result of dissolved product (Bawn, 1955)
- (iii) Additional nucleus-forming sites generated as a result of the strains caused by the entrapped gaseous product.

Since no melting of nickel azide or nickel hydroxy azide product was observed at the temperature range studied, the explanation for acceleratory region has to be sought in terms of factors (i) and (iii) only.

During ageing the surface of the primary crystallite may be perfected due to annealing causing the high-energy strained sites in the vicinity of surface irregularities, like points of emergence of dislocations and high angle grain boundaries to relax to become more stable (Young, 1966). In addition during ageing sample 3 might undergo about 1.5 percent decomposition (analysis shows that the nitrogen content decreases from 41.7 for sample 2 to 40% for sample 3). It is therefore possible for a filamentary layer of the product, nickel metal, to deposit on the surface of the crystal. Even if the decomposition takes place in the core particles the product metal atoms may migrate along the grain boundaries and accumulate on the surface where they would crystallize to form metal nuclei (Prout and Moore, 1966). It is known that dislocation cores are regions in which enhanced diffusion takes place (Hirsch, 1972) at the potential nucleus-forming sites (germ nuclei) on the surface. Once sufficient, nucleation, which is facilitated by the presence of the product metal atoms, will increase as is observed in the case of silver azide (Bartlett, et al. 1956).

It is a common observation that dehydration processes in solids give rise to cracks and channels thereby introducing large number of imperfections, mainly dislocations in solids (Young, 1966, Garner, 1939, 1955).

During ageing of sample 2 for 360 days dehydration may take place giving rise to cracks and channels thus causing the development of a large number of imperfections in the aged sample (sample 3). In addition, grinding and storage of nickel azide and / or nickel hydroxy azide for a long period, as mentioned earlier, results in some degree of decomposition of the sample. The gaseous product of decomposition, i.e, nitrogen molecules, may get trapped in the dislocation cores thereby subjecting the lattice to strain which get released by producing additional dislocations in the crystal (Herley and Levy, 1973).

The removal of -OH group from the nickel hydroxy azide during ageing produces such defects which will affect decomposition. These new dislocations, on emerging at the surface become the additional nuclei-forming sites thus enhancing the rate of subsequent decomposition. Thus during ageing there is an interplay of the processes of annealing of the existing and generation of new potential nucleus-forming sites. The overall effect of prolonged ageing on nickel hydroxy azide seems to be the decrease in

number of nucleus forming sites. Thus the activation energy required in the initial stage of decomposition of sample 3 is higher ( $147 \pm 6 \text{ KJ mole}^{-1}$ ) than that of sample 2 ( $106 \text{ KJ mole}^{-1}$ ), the fresh nickel hydroxy azide in the same region.

Appreciable decomposition of sample 3 during prolonged ageing may create a large number of vacancies which will migrate to the grain boundaries. On rapid heating to the decomposition temperature, aggregation of these vacancies takes place at the grain boundaries to form small clusters which may collapse to give dislocation rings and jogs (Tompkins and young, 1957). The stresses imposed on the lattice due to the entrapped nitrogen molecules further create more dislocations. The result is the energization of certain special sites on the otherwise annealed surface of the aged sample. Such sites, though few, will be associated with greater surface energy to facilitate the formation and growth of nuclei in the later stage of decomposition thus imposing a lower energy

Table I: Summary of Activation Energies in ( $\text{KJ mole}^{-1}$ )

Sample:	Acceleratory/Exponential Region	Contracting Volume Region
1	Exp. $147 \pm 6$	$82 \pm 3$
2	Accel. $106 \pm 3$	$106 \pm 3$
3	Exp. $150 \pm 6$	$74.3$



requirement of  $74.2\text{KJmole}^{-1}$  compared to that of  $106\text{KJmole}^{-1}$  (sample 2) in the decay period of decomposition.

## CONCLUSION

The results of the present investigation have shown the effect of (i) ageing and (ii) presence of  $-\text{OH}$  moiety, on the stability of nickel azide. Although the low energy of activation of sample 2 in the acceleratory region is unusual and cannot be easily explained, it is generally observed that nickel azide (sample 1) and aged nickel hydroxy azide (sample 3) have higher rates of decomposition and therefore less stable than sample 2, (apart from the low activation energy of sample 2 in the acceleratory region, the activation energies of samples 1 and 3 are lower than those of sample 2). It does appear that ageing of sample 2 for 360 days virtually transforms it into nickel azide thus the similarities in stability between samples 1 and 3.

Although the scope of our work does not extend to correlating the relative stabilities of these samples with such microscopic properties as order of symmetry of the lattice related to  $\lambda$ , the phenon mean free path, we have tried to relate stability to the thermal conductivity of the samples. Thermal theory of explosion postulates that a detonation regime in a solid can be sustained only when the thermal conductivity of the solid is relatively small so that heat imbalance can be maintained.

The presence of  $-\text{OH}$  moiety in nickel azide appears to increase the thermal conductivity of sample 2. It is probable that the introduction of  $\text{OH}$  moiety increases the order of symmetry of the nickel azide. It has been established that a solid with a high order of symmetry has a correspondingly high  $\lambda$  and is therefore less sensitive to impact of thermal energy. Consequently samples 1 and 3 are more sensitive to thermal impact as determined in their activation energies, although the low activation energy in the acceleratory region of sample 2 is unusual. It is necessary to carry out thermal conductivity studies of  $\text{Ni}(\text{N}_3)_2$  and  $\text{Ni}(\text{OH})\text{N}_3$  to confirm the desensitization effect of the presence of  $\text{OH}$  moiety on nickel azide. It may also be necessary to conduct explosivity tests of the samples at room temperature in order to determine their detonation regime. Once determined, in addition to the already established stability profiles of the samples a choice can then be made for use in mining and other fields of mineral exploration.

## REFERENCES

- Bagdassarian, S., 1945. Photographic sensitivity of solid azides, *Acta physiochim. URSS*, 20: 441-444.
- Bartlett, B. E; Tompkins, E. C; and Young, P. A. 1958. Photoconductivity of silver azide, *Proc. Roy. Soc. London*, A246, 206.
- Bartlett, B. E., Tompkins, E. C. and Young, D. A., 1956. Studies on Decomposition of Mercury Fulminate; *J. Chem. Soc.*, 3, 323.
- Bawn, C. E. H., 1955. In *Chemistry of the solid state*; W. E. Garner Eds; Butterwoths, London, Chapter 10.
- Erofcev, B. V., 1961. Reactivity of solids; J. H. de Boer (Ed). Butherwoths, London, 273-82.
- Erofcev, B. V., and Sviridov. 1958. Studies on the decomposition of Barium Azide; *Chem. Abstr.* 52, 1741.
- Finch, A., Jacobs, P. W. M. and Tompkins, F. G. 1954; Decomposition of silver oxalate; *J. Chem. Soc.*, 2053-60.
- Garner, W. E. 1955. *Chemistry of the solid state*, Butherwoths, London, 371.
- Herley, P. J. and Levy, P. W., 1973. In *reactivity of solids*; J. S. Anderson (ed); Chapman and Hall, London, p.389.
- Herley, P. J, Levy, P. W. and Jacobs, P. K. M. 1970. A Photomicrographic and electron microscopy study of nucleation in ammonium perchlorate. *J. Chem. Soc.*, A319: 434pp.
- Harvey, E. J. 1939. Barium azide decomposition by microscopic observation; *Trans. Faraday Soc.*, 29: 653pp.
- Hirsch, B. 1972. Reactivity of solids, J. S. Anderson et al (eds.), Chapman and Hall, London, p.337.
- Jacobs, P. W. M. and Whitehead, H. M., 1969. Decomposition and constitution of ammonium perchlorate, *Chem. Rev.* 69: 551- 590.
- Jacobs, P. W. M. and Tompkins, F. C., 1955. Studies on decomposition of  $\text{Ba}(\text{N}_3)_2$ ; *J. Chem. Phys.*; 23: 1443pp.
- Prout, E. G. and Moore, D. J., 1966. Special Technical Publication, No. 400, ASTM, 45.
- Solymosi, Z. and Bansagi, K. 1968. Thermal decomposition of lead chlorate; *Acta Chem. Abad Sci, Hungary*, 56: 337pp.
- Sood, R. K. and Nya, A. E., 1981. Thermal decomposition of nickel azide, *J. Therm Anal* 22: 231-237.
- Sood, R. K., and Alobi, N. O., 1997. Cupric Azide-A new

- detonator for mining, *Global J. of Pure and Applied Sci.*, 3, 69-76.
- Sood, R. K., Nya, A. I. and Yoganarasimhan, S. R., 1982. Isothermal decomposition of zinc azide. In thermal analysis. (Ed. Miller, B). Willey, London, 1: 680pp.
- Vander Moulén, 1961. Cited in Kolthoff and Elvings *Treatise on analytical chem. Part II*, 5, 291pp.
- Walker, R. F., 1969. Decomposition of studies of  $TiN_3$  single crystal by scanning electron micrography *Trans. Faraday Soc.* 65: 332-4pp.
- Wischin, A., 1939. Thermal decomposition of  $Ba(N_3)_2$ ; *Proc. Roy. Soc. A* 172: 314pp.
- Wohler, I. and Martin, R., 1917. *J. Chem. Soc.* 112, 383.
- Yoganarasimhan, S. R. and Tompkins, F. C., 1967. Decomposition of  $BaN_3$ ; Reports submitted to Imperial college, London, 123
- Young, D.A., 1966. *Decomposition of solids*; pergamon Press, Oxford, 182.
- Young, D. A., 1961. Ageing Studies on  $Ba(N_3)_2$ ; *Nature*, 201, 251pp.