A Kinetic Study of Hydrolysis of Polyester Elastomer in Magnetic Tape

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Abstract

A useful method for the kinetic study of the hydrolysis of polyester elastomer is established which uses the number-average molecular weight. The reasonableness of this method is confirmed and the effect of magnetic particles on hydrolysis is considered.

Introduction

Long archival lifetime is an essential property of magnetic recording tape for data storage. It is well-known that the archival life of tape depends on various factors, all of which may be important. This paper is a basic study on estimating the life of magnetic recording tape due to degradation of the binder.
Polyester elastomer is used as the binder in magnetic recording tape, and one of the factors of tape degradation is the hydrolysis of the binder. Hydrolyzed binder is adhesive and the tape with hydrolyzed binder may be sticky.
In this paper, a method of the kinetic study of the binder's hydrolysis is first established. Next, the appropriateness of this method is discussed, together with the influence of the magnetic powder.

Method and Materials

Determination of the reaction rate is necessary for estimating the tape life. Ester hydrolysis is a second order reversible reaction in which ester group and water are involved. Since there is a large quantity of water in the air, it may be assumed that the amount of water in the air is constant. Thus the rate equation of ester hydrolysis can be expressed as a function of ester concentrations only (1).

$$C_e/C_{e0}=\exp(-k't) \qquad (1)$$

C_e : Ester concentration after storage.
C_{e0} : C_e at t=0 (before storage)
k' : Rate constant.
t : Storage time

The reaction rate is calculated using the changing rate of ester concentration, but it is difficult to measure the ester concentration in polymer. The rate equation of this case can be expressed using molecular weight of polymer.
Reaction rate obtained as a function of ester concentration can be conversed into the function of molecular weight by the following relationships.
Following discussion of this conversion can be given in terms of unit weight.

Defining the number of molecule in unit weight as N and ester concentration in unit weight

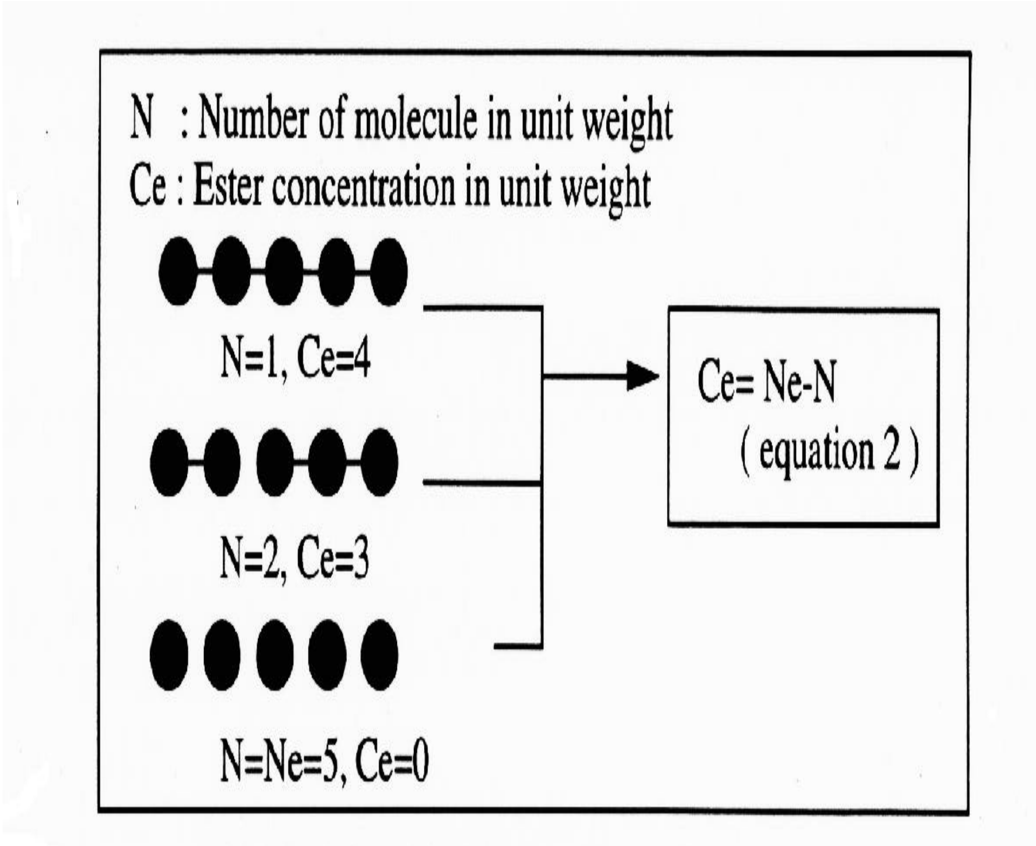


Figure 1. Relationship between N and C_e

as C_e, the relationship between N and C_e may be showed in figure 1 and represented by the following equation (2).

$$C_e=N_e-N \tag{2}$$

Ce : Ester concentration in unit weight
N : Number of molecule in unit weight
N_e : N after storage at C_e=0

Combining equations (1) and (2) leads to (3).

$$N=N_e-C_{e0}\exp(-k't) \tag{3}$$

Defining the number-average molecular weight in unit weight as M_n, the relationship between N and M_n may be represented by the following equation (4).

$$N=1/M_n \tag{4}$$

Combination of equations (3) and (4),

$$1/M_n=N_e-C_{e0}\exp(-k't) \tag{5-1}$$

(5-1) at t=0 gives (5-2)

$$1/M_{n0}=N_e-C_{e0} \tag{5-2}$$

M_{n0} : M_n at t=0 (before storage)

Eliminating N_e from equation (5-1) and (5-2),

$$1/M_n-1/M_{n0}=C_{e0}\{1-\exp(-k't)\} \tag{6}$$

Approximating exp(X) when X<<1 leads to (7).

$$1/M_n-1/M_{n0}=C_{e0}k't \tag{7}$$

Finally, redefining $C_{e0}k'=k''$,

$$1/M_n-1/M_{n0}=k''t \tag{8}$$

Equation (8) is the rate equation of ester hydrolysis expressed by number-average molecular weight (M_n) of polymer and it is used in estimating reaction rate. Equation (8) coincides with the empirical equation of Huisman [1].

The sample used in this study is normal chain polyester binder and initial molecular weight varies from 30000 to 40000. This simple structure is chosen for a basic study. Thin film made from this binder is stored in accelerating conditions, that is, high temperature and high relative humidity. After a few weeks' storage, the film is dissolved in tetrahydrofuran (THF) and the molecular weight measured by gel permeation chromatography (GPC).
The conditions of GPC are as follows:

System : Waters GPC system
Columns : Waters Ultrastyragel 500 angstrom and Linear 10^6 angstrom
Eluent : Tetrahydrofuran (THF)
Detector : Differential refractometer (RI)

Results and discussion

Figure 2 shows plots of ($1/M_n-1/M_{n0}$) vs time for storage at 30 degrees C/90% RH, 50

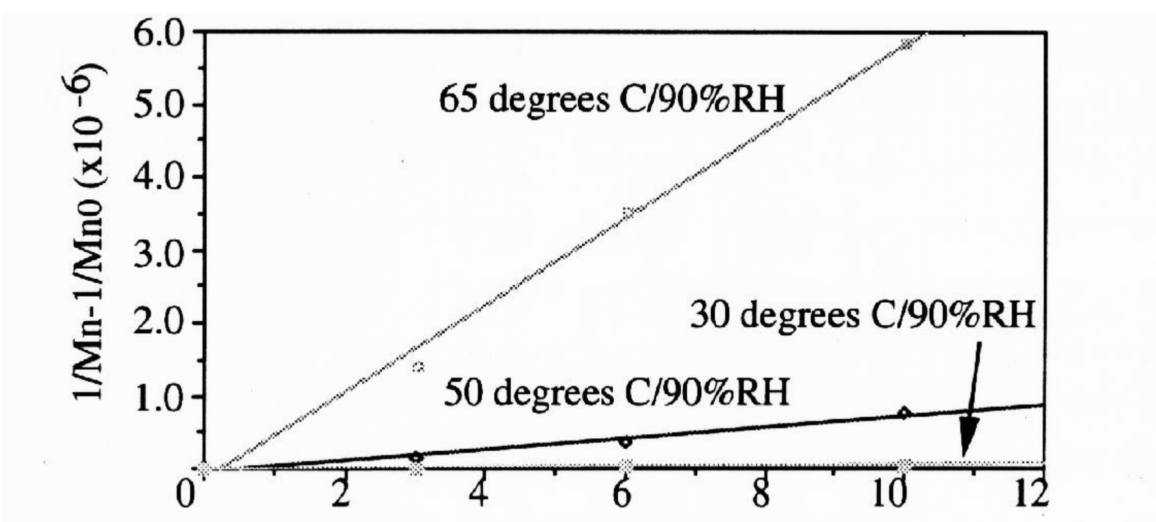
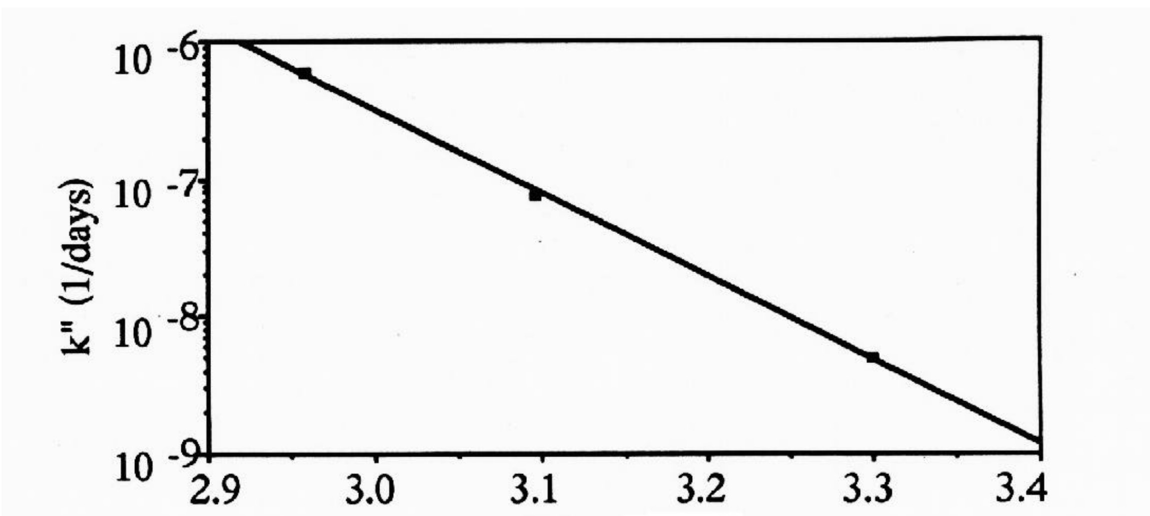


Figure 2. Variation of molecular weight in 90% RH

degrees C/90% RH and 65 degrees C/90% RH. These plots show that $(1/M_n - 1/M_{n0})$ is proportional to time and confirm the rate equation (8). The reaction rate constants which are the slopes of the plots increase as the temperature increases. Table 1 shows the rate constants at 90% RH which are calculated from the plots of Figure 2.

Table 1. Rate Constants at 90% RH

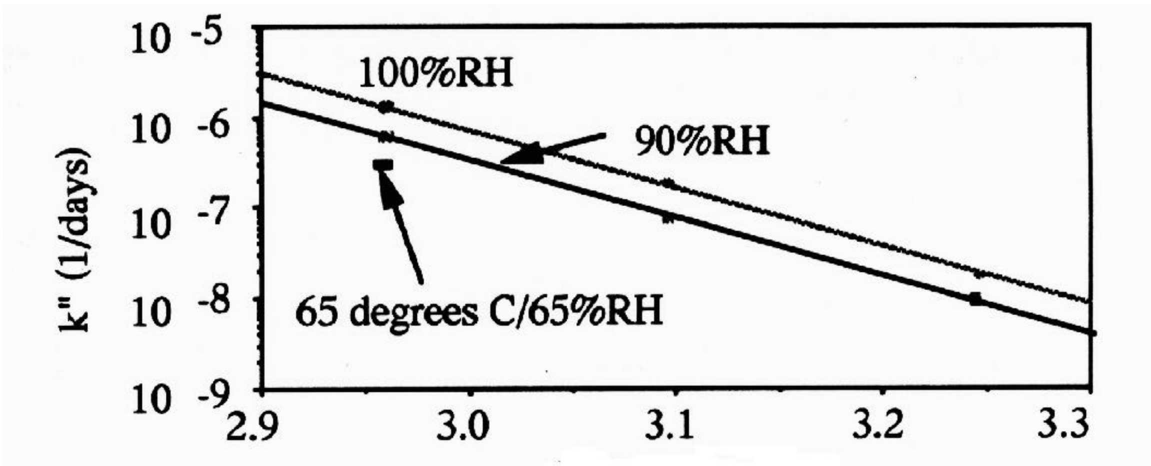
Temperature (°C)	Rate constants k” (1/days)
30	5.0×10^{-9}
50	7.6×10^{-8}
65	6.0×10^{-7}



1/T ($\times 10^{-3}$ K)

Figure 3. Arrhenius plots of polyester binder in 90% RH

Figure 3 shows the Arrhenius plot of the rate constants. An activation energy is calculated from Arrhenius' equation and it is about 110 kJ/mol. Now we can estimate the rate constants at various temperatures when the relative humidity is constant at 90%.

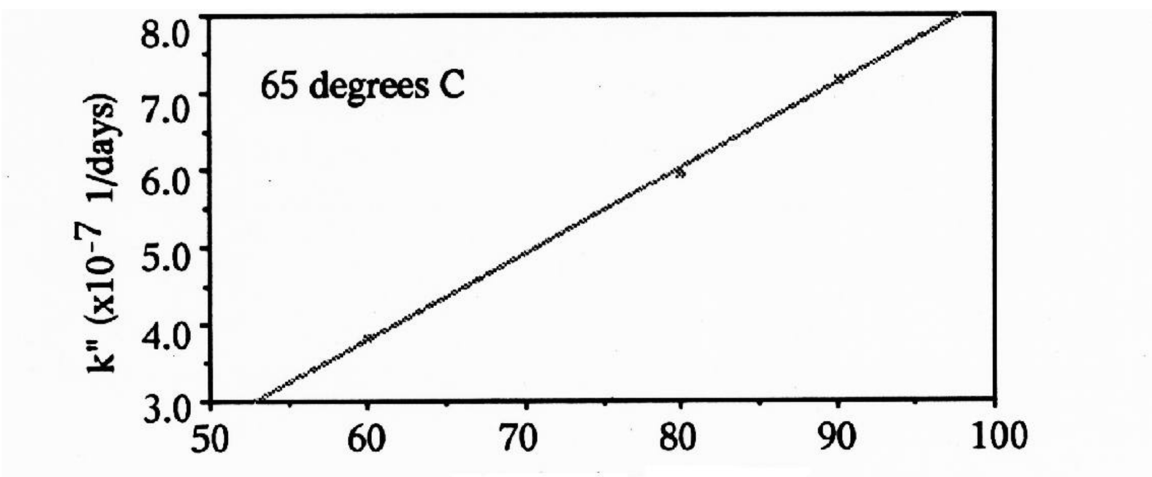


1/T (× 10^{-3} K)

Figure 4. Arrhenius plots of polyester binder in various humidities.

Figure 4 shows Arrhenius plots in other humidities. Activation energy is not dependent on relative humidities.

Figure 5 shows relationship between rate constants and relative humidities at 65 degrees C.



Relative humidity (%)

Figure 5. Effect of relative humidity on rate constants (k”)

Relative humidities and rate constants are in proportion. The reason for this is that the sample films are so thin that moisture diffuses rapidly. Equation (9) derives from (8) in consideration of this effect.

$$(1/M_n-1/M_{n0})/H=k^*t \qquad (9)$$

H : Relative humidity

Rate equation (9) exhibits the effect of relative humidity.

The effects of storage temperature and humidity on the hydrolysis of polyester are clarified. Thus we can estimate the reaction rate in every environment. Half value periods of molecular weight can be estimated.

Table 2. k”, k’ and half value periods of molecular weight (M_n)

Temp.	% RH	k”(1/days)	k’ (1/days)	Half value period (years)
20	65	8.0×10^{-10}	1.2×10^{-11}	110
30	60	4.1×10^{-9}	$5.0\text{-}7.0 \times 10^{-11}$	15.0-25.0
30	90	4.9×10^{-9}	$5.0\text{-}7.0 \times 10^{-11}$	15.0-25.0
40	60	1.7×10^{-8}	$2.0\text{-}3.0 \times 10^{-10}$	4.0-5.0
40	90	2.0×10^{-8}	$2.0\text{-}3.0 \times 10^{-10}$	4.0-5.0
50	60	6.3×10^{-8}	$8.0\text{-}11. \times 10^{-10}$	1.0-1.5
50	90	7.6×10^{-8}	$8.0\text{-}11. \times 10^{-10}$	1.0-1.5
65	60	3.9×10^{-7}	$6.0\text{-}7.0 \times 10^{-9}$	0.1-0.2
65	90	5.9×10^{-7}	$6.0\text{-}7.0 \times 10^{-9}$	0.1-0.2

Table 2 shows rate constant and predicted half value periods of molecular weight. The hydrolytic speed of 65 degrees C/90% RH is about 1000 times that of 20 degrees C/65% RH.

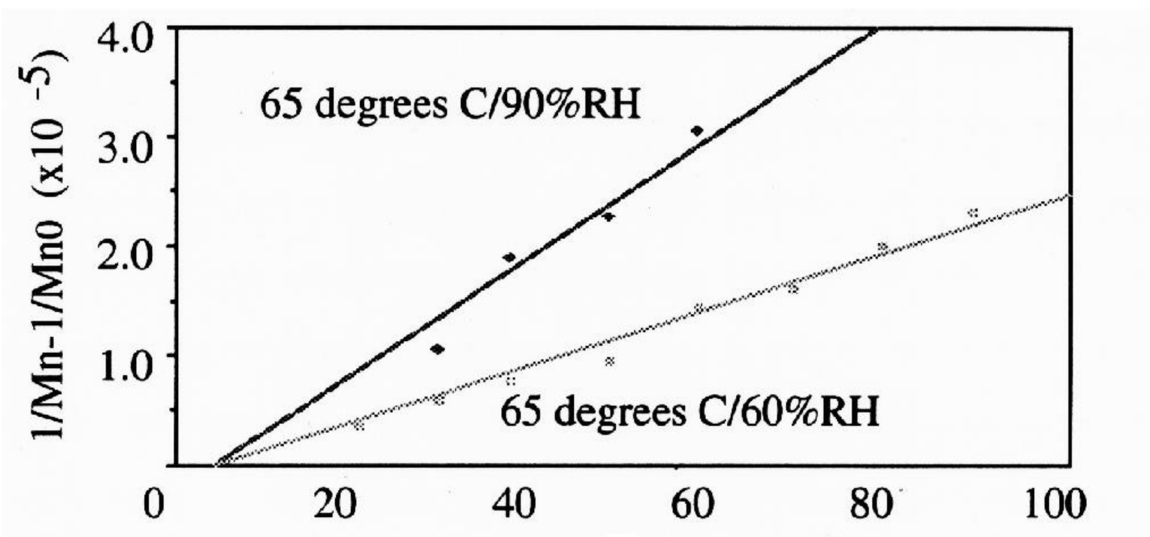


Figure 6. Confirmation of half value periods

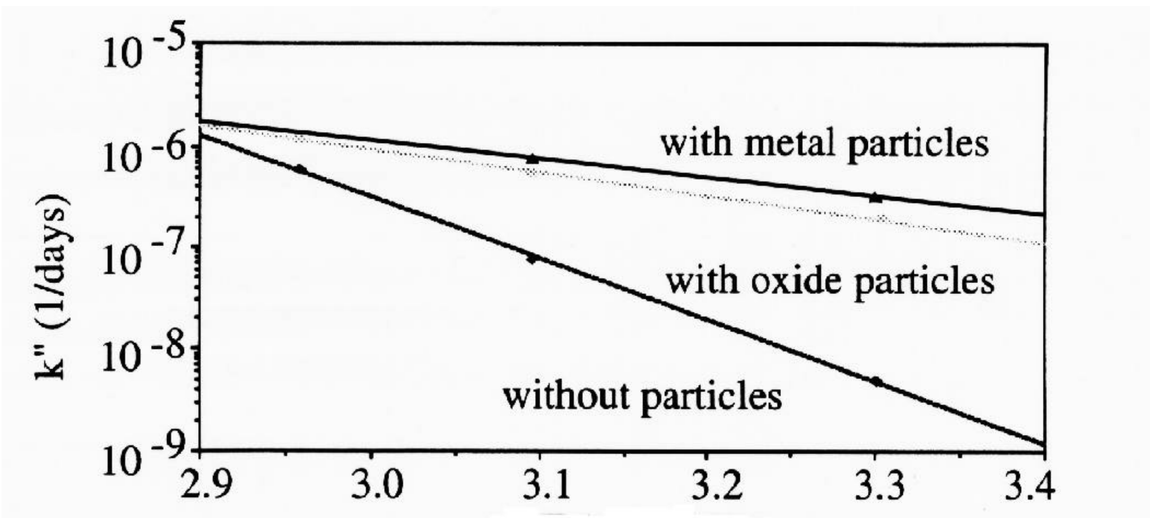
For example, half value periods of molecular weight of this sample are estimated to be about 100 days at 65 degrees C/60% RH and 50 days at 65 degrees C/90% RH. The number of days was confirmed by storing until the molecular weight decreased to half value. Figure 6 and table 3 show the data.

Binder and magnetic particles are principal ingredients of the paint of magnetic tapes. We found that the presence of magnetic particles reduced activation energy. Figure 7 shows

Table 3. Molecular weight (M_n) of binder stored until half value period

Time (days)	65°C/60% RH	65°C/90% RH
0	39041	39041
9	35847	37367
29	31667	27620
37	29975	22419
48	28495	20730
58	24909	17781
69	24002	
79	21880	
89	20512	

comparison of Arrhenius plots of polyester binder with metal particles, with oxide particles and without particles. Activation energy decreases when magnetic particles are mixed with



1/T (× 10^{-3} K)

Figure 7. Comparison of Arrhenius plots of k" with and without magnetic particles

polyester. Catalytic action by magnetic particles is shown by these data. This shows that ester hydrolysis is accelerated by catalytic action of magnetic particles.

Catalytic action disappeared in the case of binder with magnetic particles covered with

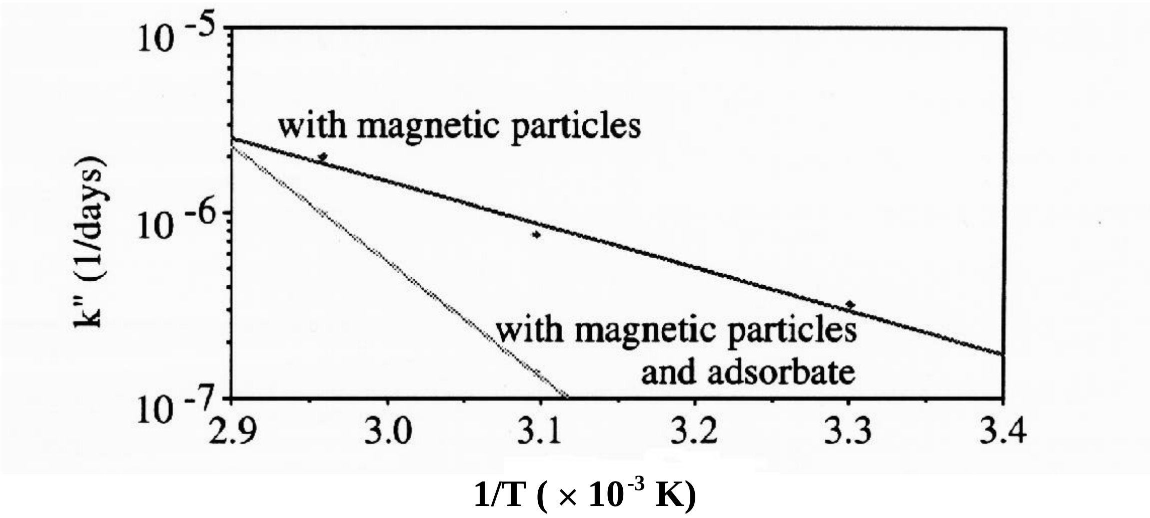


Figure 8. Comparison of Arrhenius plots of k” with and without adsorbate

adsorbate citric acid or the like, shown in figure 8. The decrease of activation energy is not observed for the binder with magnetic particles covered with citric acid. It is supposed that such catalytic action occurs by interaction of activation points of the magnetic particles and binder adsorbed at the points. Thus the catalytic action disappeared when the activation points were covered with adsorbate.

Conclusions

1. We established useful method for the kinetic study of the hydrolysis of polyester elastomer in magnetic tapes. Using number-average molecular weight (M_n), the rate equation of polyester hydrolysis led to the equation $(1/M_n-1/M_{n0})/H=k^*t$.

2. Catalytic action by magnetic particles is demonstrated and it is supposed that such catalytic action occurs by interaction of activation points of magnetic particles and binder adsorbed at the points. The catalytic action disappeared when the activated points were covered with adsorbate.

3. We make use of this method and these results to estimate the life of magnetic tape.

References

H.F.Huisman.,et.al. "Aging of Magnetic Coatings" PD Magnetics B.V., Oesterhout, NLD, 16(2), 177-195(1988) [1].