The storage stability of metal particle media : Chemical analysis and kinetics of lubricant and binder hydrolysis

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Abstract

Archival life of MP (metal particles) tape is one of the biggest concerns for mass data storage users. The long-term stability of a MP tape is studied in terms of lubricant and binder systems. MP formulation tape that has been used for M2 videotape and DLT3 tape for more than fourteen years is analyzed. Gas chromatography (GC) and gel permeation chromatography (GPC) are used to analyze chemical changes of lubricant, fatty acid ester, and binder, polyester-polyurethane. The kinetics of hydrolysis of the fatty acid ester can be described by two first-order reactions. One is estimated to be corresponding to the hydrolysis of fatty acid ester on the surface of the magnetic layer, and the other to the fatty acid ester dissolved in the binder of magnetic layer. The hydrolysis of polyester-polyurethane (PU) can also be described by a first-order reaction. A durability test reveals that this MP tape keeps its good performance after long-term storage. A magnetization decrease of about twelve percent is observed after saving for fourteen years. This small decrease does not affect the above mentioned good performance.

1 Introduction

MP tape has been widely used in the fields of mass storage, broadcast, etc. In these fields, storage stability of MP tape is very important together with recording density. For development of MP media excellent in storage stability, it is necessary to know the problems in long-term storage. The claims during the use were investigated, and it became clear that many of them were due to the hydrolysis of the fatty acid ester as lubricant and the PU as binder.

As the first step of estimation of life expectancy of media, it was decided to study chemical changes of organic materials of MP formulation tape that has been used for M2 videotape and DLT3 tape for more than fourteen years. In addition, the magnetic properties and other physical characteristics were investigated and the durability was tested.

2 Experimental

The MP tapes for M2 stored in a laboratory for more than fourteen years were analyzed. Two types of fatty acid ester are contained as lubricants in the tape. One fatty acid ester is buthoxyethoxyethoxy stearate (BE2S) and the other is isoamyl stearate (AS). They were extracted with n-hexane from the tape and were quantified by GC (Shimadzu GC-17A).

Analysis of binder was also performed. Polyvinyl chloride and PU are contained as binder in the tape and they are crosslinked by hardener. PU used in a magnetic layer of this tape consists of methanediphenyl diisocyanate, hydroxycaproic acid, neopentyl glycol and phthalic acid. The magnetic layer was removed mechanically from magnetic tape and the soluble components were extracted with tetrahydrofuran. The extracts were analyzed by GPC (Toso HPLC8020) with an ultraviolet detector. Polyvinyl chloride shows no absorption in the ultraviolet region and only PU can be quantified.

3 Results and Discussion

3.1 Fatty acid ester

It was reported that lubricant loss in short term accelerating conditions is due to degradation and vaporization[1][2]. In our study, the decay of lubricant in long-term natural storage was investigated from a viewpoint of hydrolysis. It is known that the hydrolysis reaction of ester is first-order to ester concentration if enough water exists. The amount of fatty acid ester which remains in the tape and can be extracted with n-hexane is shown in Fig.1 and the decay rate constant of fatty acid ester is shown in Fig.2 and Tab.1.

The decay reactions of the two fatty acid esters are expressed as two first-order reactions of two steps in which each reaction rate differs. The ratio of reaction rate of BE2S to that of AS is shown in Tab.2. In the first step, although AS is smaller and more volatile than

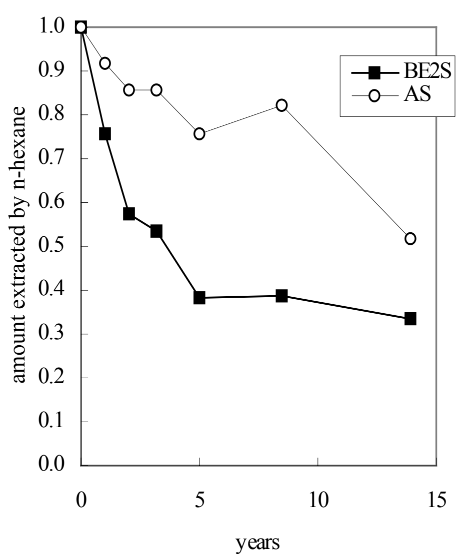

Fig.1 Decay of Fatty Acid Ester

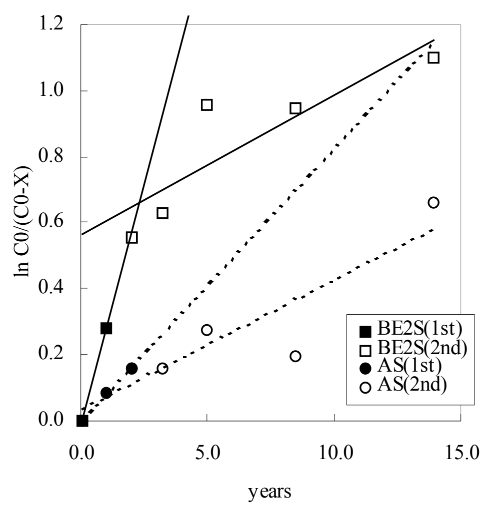

Fig.2 Reaction rate of Fatty Acid Ester
C0;initial amount
C0-X;remaining amount

BE2S, the decay loss reaction rate of BE2S is about 3.6 times of that of AS. This ratio of reaction rate is approximately equal to the ratio of hydrolysis reaction rate of fatty acid esters measured in acetone containing a small amount of HCl. Therefore it is considered that hydrolysis reaction is dominant in the first step. In the second step , the reaction rate of BE2S is about 1/6 of the first one and the difference of reaction rate of BE2S and AS is small, so vaporization is considered to be involved. It is assumed that the first decay

	/year	/sec
BE2S (1st)	2.9E-01	9.3E-09
BE2S (2nd)	4.3E-02	1.3E-09
AS (1st)	8.2E-02	2.6E-09
AS (2nd)	3.9E-02	1.2E-09

Table 1. The Decay Rate Constant of Fatty Acid Esters

1st	2nd	In acetone solution made weakly acidic with HCl
3.6	1.1	3.1

Table 2. The Decay Rate Ratio of BE2S/AS

comes from the fatty acid ester on the magnetic layer surface and the subsequent slow decay comes from the fatty acid ester dissolved in the magnetic layer binder. The thickness of the fatty acid ester layer on the surface is calculated to be about 0.7 nanometers from the quantity lost at the first step reaction and the surface area of the tape measured by gas-adsorption method. The concentration of the fatty acid ester dissolved in the magnetic layer binder is also calculated to be about 3 wt%, and is equal to the concentration at which binder films become opaque when the varying amount of fatty acid ester is added.

3.2 Polyester-polyurethane

/year	/sec
4.8E-06	1.5E-13

Table 3. The Decay Rate of Polyester Polyurethane

Though hydrolysis of PU of magnetic tapes had been reported [3][4], PU of MP tape in long-term natural storage was not yet investigated. We attempted to obtain the reaction rate of hydrolysis of PU using the ratio of the soluble component to PU content and the number average molecular weight of soluble PU. If one ester linkage of polymer is broken by hydrolysis, the number of PU molecules increases by one[5]. In order to find the hydrolysis reaction rate, the reciprocal of number average molecular weight was used

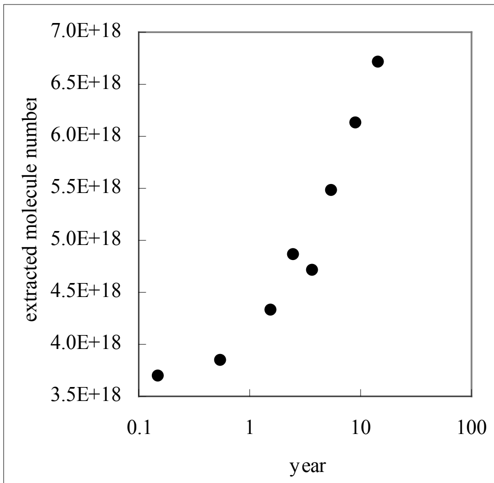

Fig.3 Molecule Number of Soluble PU
extracted from magnetic layer 1g

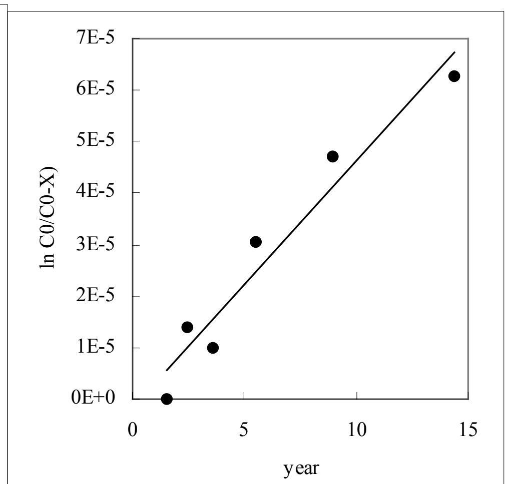

Fig.4 Reaction Rate of PU Degradation
C_0;total ester linkage number in PU
X;ester linkage number broken
(=increased molecule number)

as the number of soluble PU molecules. The number of soluble PU molecules is shown in Fig.3. The number of soluble PU molecules increased remarkably after about 2 years, and hydrolysis reaction was considered to become predominant. Hydrolysis reaction rate was calculated using the increase of the number of molecules, as a first-order reaction shown in Fig.4 and Tab.3. The hydrolysis reaction of PU is extremely slow when compared to the hydrolysis of fatty acid ester in this magnetic tape. The reason is considered to be because PU is a high polymer and is crosslinked by hardener.

3.3 Physical characteristics and Durability test

Physical properties and video output level of a new tape and the tape stored for 14 years were measured and were compared in Tab.4. A 1-minute length x 1,000 passes running test using an M2 VCR was also performed as a durability test. Though remanence magnetization loss was about 12 % after 14 years, the decrease of video output level was 0.6 dB and was acceptable in practical use. The glass transition temperature of the magnetic layer did not change. The friction coefficient of the magnetic surface increased slightly but kept at a low value. After running for 1,000 passes as the durability test, the slight debris on the video heads was observed. But there was no difference between these two tapes in the amount of debris. These tests reveal that this MP tape keeps its good performance after long-term storage.

Storage Time (years)	0	14	Test Method
Magnetic Properties Br (Gauss)	2,640	2,320	VSM
Mechanical Properties Glass transition temperature of magnetic layer (degree at Celsius) Friction coefficient of magnetic surface	82 0.22	82 0.31	Dynamic viscoelastometer Vs. Stainless bar
Electro Magnetic Conversion Properties Video output (dB)	0	-0.6	M2 VCR

Table 4. Changes of Properties of MP Tape after Long-Term Storage

4 Conclusions

The physical characteristics and the chemical changes of the MP tape over 14 years were pursued, and the storage stability of the MP tape was proved to be satisfactory. The hydrolysis reactions of lubricant and binder in the MP tape could be expressed as first-order reactions, and the reaction rates were calculated. It becomes possible to make a quantitative comparison between the changes in the natural storage conditions and those in the accelerating tests. The thickness of surface fatty acid ester of the magnetic layer and the concentration of fatty acid ester dissolved in the binder can be estimated. Usually,these are very difficult to quantify by other techniques such as ESCA or AES because fatty acid esters are volatile and have no special element except carbon, hydrogen and oxygen in common as magnetic layer binder elements[6].

The accelerating conditions which can be used to simulate more precisely the passage of long time on the basis of these data will be established and be applied for the development of new media.

References

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