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Stability of Metal Particle and Metal Particulate Media

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1. Introduction

Metal particulate (MP) video tape was launched for 8 mm video tape in 1985. Since then MP tapes have been applied to several consumer formats and instrumental formats because of its superior electrical performance. Recently data storage media, such as DDS, and D - 8, have started employing MP tape.

However, there are serious concerns with archival stability of MP tape particularly in the case of data storage use, as metal particles essentially have problems with chemical instability and are susceptible to oxidation and corrosion. Although there have been some studies about the archival stability of metal particles or MP tapes [(1) ~ (3)], a clear understanding has yet to be reached.

In this paper, we report the stability of magnetic properties of current metal particles, and then discuss the new technologies to improve the stability further.

2. Stability of Current Metal Particles

A metal particle is composed of three layers. Pure iron core with σs=222 emu/g is covered with a passivated iron oxide layer, and it is covered again with a ceramic layer composed of Al $^{and}/_{or}$ Si compounds. The outer two layers prevent the oxidation of the iron core. The important role of the surface ceramic layer to the stability of metal particles is shown in Fig. 1.

The stability of metal particles is improved still more when they become part of the tape, since they are covered uniformly with binder molecules during the mixing process (Fig. 2). Fig. 3 shows the archival stability of the RF-output of Betacam tape. Little degradation is observed even after long term storage in a 45°C, 80%RH environment. So, from a practical viewpoint the current MP tape has sufficient stability due to the multilayer protection of the iron core.

3. Newly Developing Technologies

3-1. Dense Oxide Layer

The morphology of pure iron core is thought to be measured with X-ray crystallite size Dx. The aging effects of σs and Dx of current metal particles under 60°C, 90%RH environment is shown in Fig. 4. The initial degradation of σs occurs without damage to the morphology of iron core. This fact indicates that the degradation of σs begins with the destruction of the oxide layer. Therefore the formation of a uniform and dense oxide layer would promise improvement in the stability of metal particles.

Fig. 5 shows the comparison of the degradation ratios of flux density between current MP tape and improved MP tape which utilizes new metal particles with a dense oxide layer under the storage conditions of 65°C, 90%RH. The improved MP tape is twice as stable as the current one which is already stable.

3-2. Anticorrosive Agent

In order to improve the archival stability to the highest degree possible, we are researching anticorrosive agents. A low molecular organic compound would be selected as an anticorrosive agent to minimize the decrease of magnetization by the use of non-magnetic materials. The organic anticorrosive agent which is adsorbed onto the surface of the metal particles changes the hydrophilic surface into a hydrophobic surface and cuts off direct contact with oxygen and moisture in the atmosphere.

The results of the aging test of the currently used metal particles, the improved ones (with a dense oxide layer), and the anticorrosive agent treated particles are shown in Fig. 6. The stability of metal particles are amazingly improved through the application of the anticorrosive agents. The degradation ratio of treated metal particles is comparable to that of magetite particles which have the same size.

4. Stability of Coercivity

The coercivity of metal particles usually shows almost no change or a little increase from the aging test. The degradation of coercivity, however, is observed only when the magnetization decreases extremely.

5. Conclusion

Currently used metal particles are stable, as they have protection layers of ceramic coating and passivated oxide. Therefore the MP tape has sufficient stability for practical use. In order to improve the stability further, new metal particles which have a uniform and dense oxide layer and an anticorrosive agent are under development.

References

(1) T. D. Lee, S. Hu and N. Madulid; IEEE Trans. on Magn. MAG-23 (1987) 2880

(2) D. E. Speliotis; IEEE Trans. on Magn. MAG-26 (1990) 124

(3) Y. Yamamoto, K. Sumiya, A. Miyake, M. Kishimoto and T. Taniguchi; IEEE Trans. on Magn. MAG-26 (1990) 2098

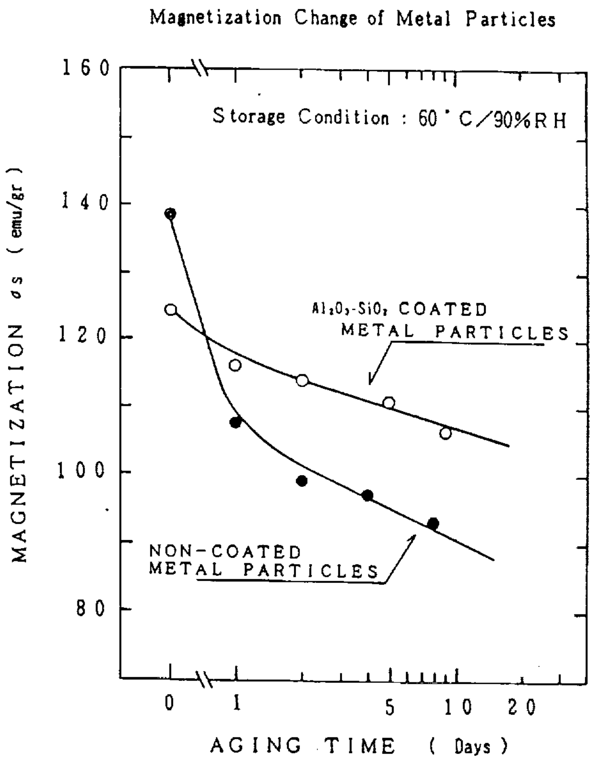
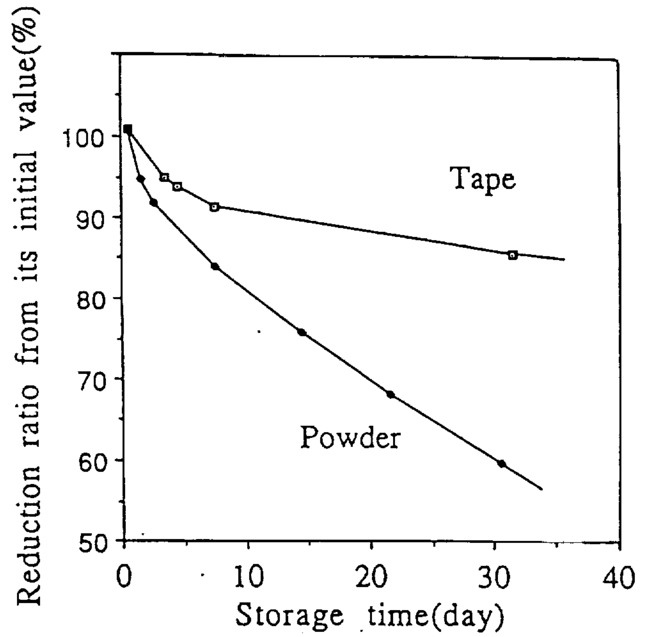


Fig. 1



Storage condition ; 60°/90%RH

Fig. 2

SONY

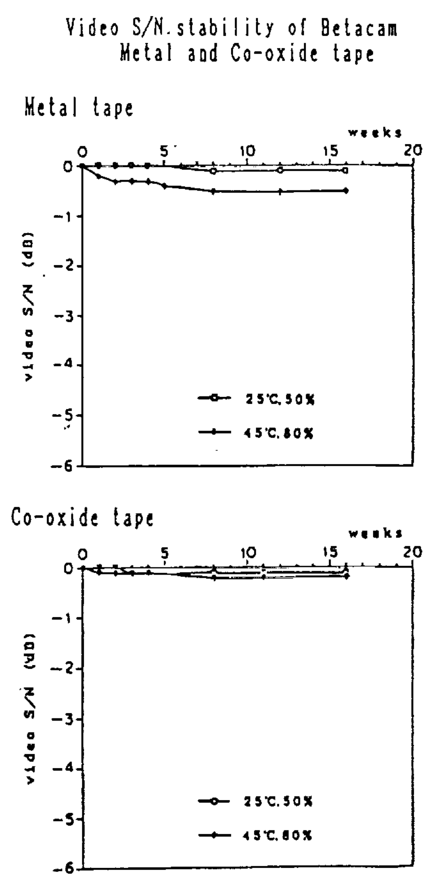
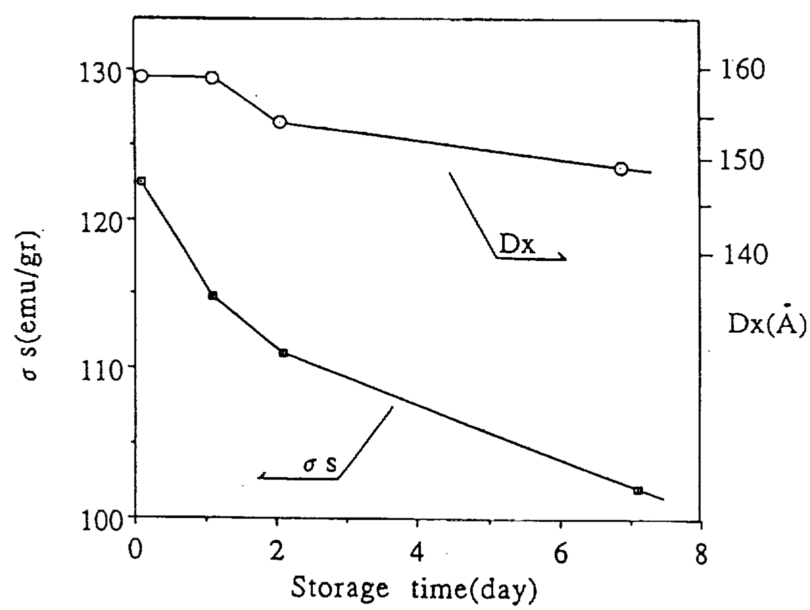
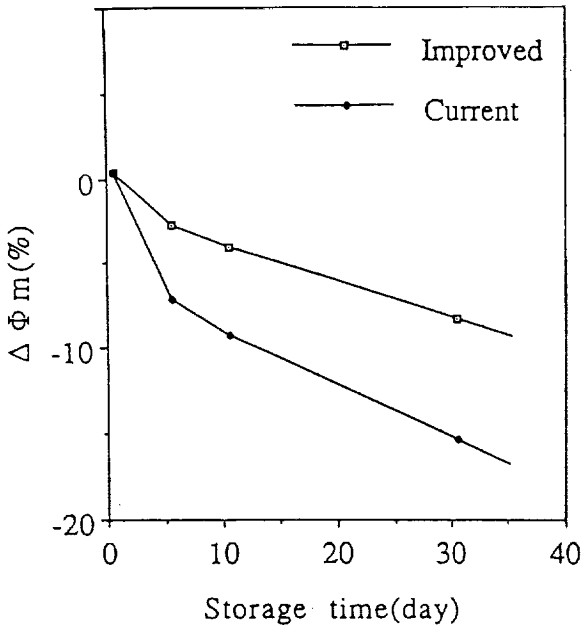


Fig. 3



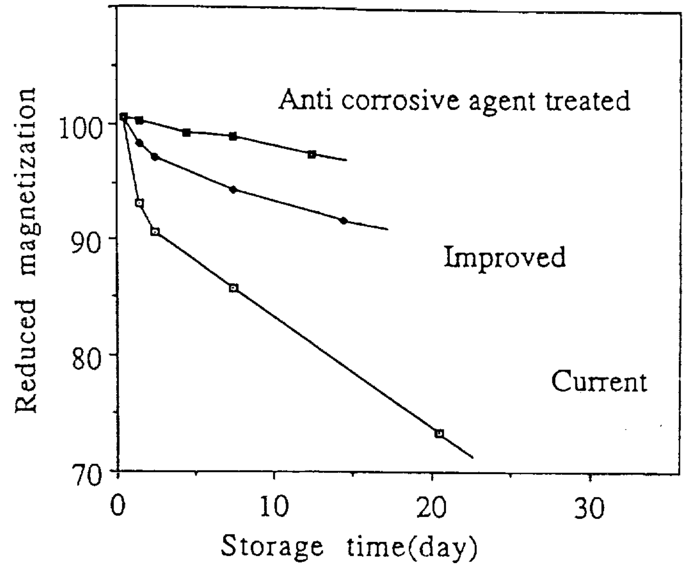
Storage condition ; 60°/90%RH

Fig. 4



Storage condition ; 65°／90%RH

Fig. 5



Storage condition ; 60°／90%RH

Fig. 6

Surface Treatment of Organic Anticorrosive Agent

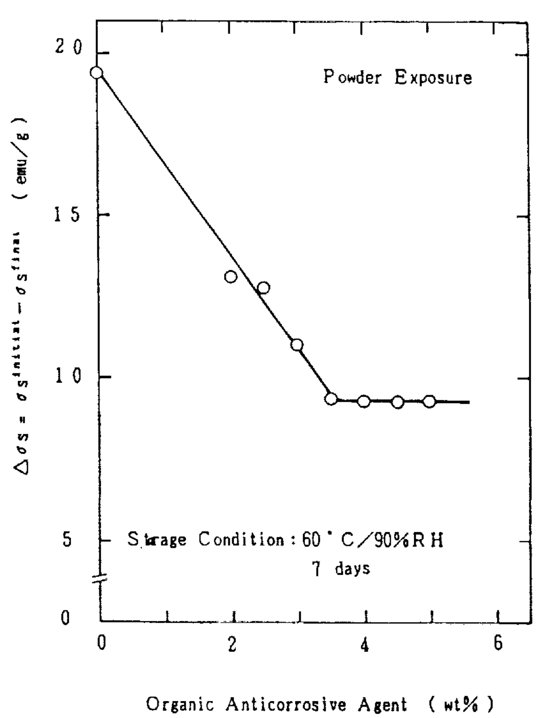


Fig. 7

DR. KRYDER: Next, we have a two for one deal. Ampex is going to split their time between two speakers; they promise to keep both their talks within the 15-minute time limit.

The first talk will be by Allan Hadad. Allan has a B.S. Degree in Chemistry and an M.S. Degree in Materials Engineering. He started his professional career as a synthetic organic chemist working in the application of high-performance polymers in the wire and cable industry.

Allan began working in the recording industry in 1974 as a formulation development chemist. He has developed various tape formulations for both consumer and professional use. He has participated in the application and introduction of products based on the evolution of new magnetic materials, from cobalt-adsorbed iron oxides to iron particles.

Allan has also managed Ampex's metal-evaporated tape program. Allan's current assignment is Manager of Formulation Development for Ampex Recording Media Corporation in Redwood City, California and Program Manager for an all metal particle development effort in both Redwood City and Opalaica, Alabama.

Allan will be speaking on an empirical approach to predicting archival stability and primarily discussing metal particles.

AN EMPIRICAL APPROACH TO PREDICTING ARCHIVAL STABILITY

Mr. Allan Hadad
Ampex Corporation

MR. HADAD: Good afternoon. Of course, John and I are going to be splitting the time; but we never did come to an agreement about where the split would be. So, since I'm here first --

(Laughter)

MR. HADAD: I would also like to thank Dr. Hariharan for inviting me. He called me about a month ago; he asked me what I thought about the concept of free speech. I said I agreed with it; and he said: Good. I'd like you to give one at this conference. So, here I am.

(Laughter)

(Showing of viewgraphs)

MR. HADAD: I would like to talk about the stability of high-density media, particularly of course metal particles, that I have been involved with pretty much since 1978.

I like to separate environmental stability from archival stability. I feel that most of the testing that we have done so far--and much of the data that you have maybe even seen today--is environmental stability, discrete conditions in which tapes have been exposed. You have seen some data. I call that a user condition, perhaps during acquisition, as opposed to long-term storage.

Archival stability, I think, has to be determined by predictive techniques, mathematical modeling, taking a lot of data from a variety of environmental exposure conditions, sort of lumping it together and building an expression, to be able to predict what will happen at any temperature and humidity condition.

What will the environmental stability of a tape be? How long will it really last? What's the lifetime of tape?

So, what I am going to present here is some data that we have acquired on environmental stability, basically to give the users confidence that under a certain variety of conditions, we feel very confident ourselves that metal particles do produce a viable recording medium for high- density information.

I will follow that then by an empirical approach that we have developed and are trying to propose as really the means or the vehicle to predict what the lifetime of tape will be.

(Change of viewgraph)

MR. HADAD: When we first got into the metal particles, we worked initially a great deal with the particle manufacturers themselves. They have made a lot of changes for us, as well as for all the other magnetic tape manufacturers, to produce much more stable particles, more passive particles.

Just some data that we've got. It was collected between 1987 and 1990. Three different particles that have been evaluated in our laboratory since 1987; and basically, the conditions are essentially ambient: 22^{o} C/40% relative humidity.

As you can see, obviously there are a variety of materials available from the particle manufacturers; but in general, what we are seeing here is that after three and a half years--and this is naked tape; it is not protected by a cassette case

(Change of viewgraph)

MR. HADAD: Tapes exposed to the ambient environment that, after three and a half years, have experienced losses of about or less than 2 percent in B_m.

(Change of viewgraph)

MR. HADAD: Going a little further then, looking at some of those environmental exposure conditions, I've got a chart here. We are looking at four different tapes, commercially available tapes--some of our own, some of our competitors--at three different environmental conditions.

Ambient again, 30° C, 70% relative humidity, and 54° C, 85% relative humidity--fairly extreme conditions. Although I believe that certain users may for short periods of time have exposed the tapes to these conditions, especially during initial acquisition of data, or perhaps through transient activities, as Darlene said--a fire, a sprinkler system going off--that often tapes can be exposed to some of these more extreme conditions.

The bottom line: the loss in B_m. Obviously, for ambient conditions again, we see some variation; but basically, around a 1 to maybe a 3 percent loss, after nearly six months exposure.

Moving up to the 30° C /70% relative humidity, losses on the order now--it depends on the manufacturer--around 2 to 3 percent loss in B_m again.

And then finally, the very extreme case, where now we start to see very rapid or much more devastating losses in magnetic performance, although again we wouldn't certainly call that an archival or storage condition.

Now, perhaps for certain short amounts of time, and it could be tolerated maybe on up to six months, or maybe a couple of weeks, in an environment like that, that data could be collected; and acceptable losses in magnetic performance would occur.

(Change of viewgraph)

MR. HADAD: Going out a little bit further, some D-2 tape, again under ambient conditions, six months worth of data. And we see somewhere around a 1 dB loss after 24 months--two-year data now.

In this case now, we are looking at tapes that are protected by the cassette. We are moving a little bit further along now where, on the tapes themselves, there is an extra level of shielding. Of course, the particles degrade the fastest; we saw some of that in the paper given by the gentleman from Sony.

We put it into the tape system; the binders give it a degree of shielding. Now, it's inside a cassette. There is an additional degree of shielding. Two-year data then, around a dB loss under ambient conditions for this particular sample.

Of course, there is one thing about all of this. If you look at two and three-year data, that's the old stuff now--right? Improvements have been made since.

(Change of viewgraph)

MR. HADAD: A real quick look at errors. This seems to be the real key. Again, about six-month data and essentially with some variability of three of these samples at ambient conditions, 22^{0} C/50% relative humidity, with no dramatic change in the errors per frame here with three of the manufacturers.

One of the tapes here apparently had some debris on it that was actually being removed with the repetitive testing over a period of time. Of course, we have seen that before.

(Change of viewgraph)

MR. HADAD: Under more extreme conditions there is an increase in errors, again cassettes. We've got one here--actually, it was the same one that was cleaning up-- but fairly ragged out here at the end.

But in general again, no real change in the error count at 30^{0} C/70% relative humidity for a period of almost six months.

Okay. That's environmental stability. That's not really kinetics. As a chemist and as a materials scientist, I like to reduce things down to mathematical expression and predict: How long will these tapes really last under normal storage conditions?

We have to come up with a coefficient that relates; you can sort of additively combine all the exposure conditions and determine how much time is really left on this tape.

(Change of viewgraph)

MR. HADAD: My favorite chart is the psychrometric chart. For those of you who have not seen it, it basically relates temperature to water content in air. Relative humidity are the curved lines. Absolute humidity are the horizontal lines.

What we have done is through an experimental design, these points are actual conditions that we have exposed powders to. Now, you start at the front end, and you adjust the powders themselves; there are about 12 conditions here. You have to do a multitude of testing.

Powders are subjected to these temperature/ humidity combinations for periods extending up to several months. Data is collected periodically; a curve is drawn of the degradation behavior and the slope of that line is determined. That's the degradation rate.

Those degradation rates at each of these points we will put into the computer, crunch it, and a mathematical equation was generated, describing -

(Change of viewgraph)

MR. HADAD: degradation rate as a function of, in this case, the silicon content of the powder that we are looking at as a variable, relative humidity and temperature, cross products between those and the square terms.

(Change of viewgraph)

MR. HADAD: We have a nonlinear equation that allowed us to generate lines of constant degradation rate, if you will, as a function of temperature and humidity for a given particle and gives us the ability now to predict long-term behavior at any temperature/humidity combination within the experimental region.

What these numbers are, again, are lines of constant degradation rate. One thing it shows is, that the relative humidity is the big driving factor in degradation of iron particles; temperature is not as great a factor until you get below this critical value here whereas say, you increase temperature, degradation rate does increase.