Storage, Preservation, and Recovery
of Magnetic Recording Tape

by

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ABSTRACT

During the 1970's, a commercial magnetic recording tape fabricated with magnetic oxide particles, and with oxide and backcoat binders made from polyester urethane was being used for spacecraft tape recorders, and which would periodically manifest operational problems such as layer-to-layer adhesion, stick-slip, and shedding of sticky organic materials. These problems were generally associated with periods of high humidity. An experimental study identified that these problems resulted from hydrolysis of the polyester urethane binders. Hydrolysis is a chemical reaction involving water, and polyester urethane elastomers are very susceptible to hydrolysis. This same study further identified that binder hydrolysis, and not binder oxidation, or environmental degradation of the magnetic oxide particles, was the primary chemical aging mechanism of these tapes resulting from exposure to the ambient environment. For those tapes using some or all polyester urethane elastomers in the binder formulation, the study resulted in a capability to specify safe environmental conditions for tape use, to select long-term archival storage environments for chemical preservation, and to develop procedures for recovery of tapes degraded from exposure to water or high humidity.

INTRODUCTION

Magnetic recording tapes enjoy widespread use as recording medium ranging from home and personal use to the entertainment industry, and for many diverse business, archival and scientific applications. Even as new and impressive technologies for recording audio and video information continue to be developed and marketed, significant. quantities of recording tapes with valuable information already reside in libraries and archival storage areas worldwide. The tapes being described in this article are those fabricated with magnetic oxide particles (gamma-ferric oxide) , and with polyester urethane elastomers as organic binders. These tapes became available as common, commercial tapes in the 1960's, and are still available today. It is reasonable to assume that most tapes recorded since the 1960's and currently in libraries and archival storage are almost likely to contain polyester urethanes.

For virtually all applications, such tapes perform exceptionally well, without user complaint, but occasionally problems are encountered. Chief amongst the problems are manifestations related to the tapes becoming sticky, and in some cases, to the tapes shedding gummy and tacky materials which can spread undesirably over various mechanical components of tape drive and recording equipment. These gummy products can lead to increased error rates during tape operations . A common feature generally associated with these problems has been a history of tape exposure to a humid environment.

The tapes being described are composed of approximately 20 wt.% magnetic oxide particles and 80 wt.% polymeric materials. With the exception of recording properties which are ascribable to the magnetic oxide particles, almost all of the rest of tape properties important to performance, handling, storage, and environmental stability (aging) are related to the polymeric constituents of tape. At ambient temperatures, magnetic oxide particles are chemically stable to oxygen and atmospheric moisture, but the polymeric materials may not be. The aging of magnetic recording tape with magnetic oxide particles, and therefore storageability and preservation, is related to the nature and the rates of chemical reactions which occur between the polymeric constituents of the tape and atmospheric oxygen and moisture. Any environmentally caused chemical deterioration of the polymeric constituents of tape will affect their physical and mechanical properties, and which will in turn significantly impact tape performance, operational life, and archival storage.

Figure 1 illustrates the basic construction and components of the common magnetic recording tapes being described. These tapes consist of a thin (from 6.3 to 38.1 microns) plastic film substrate with an oxide coating and, for some tapes, an additional backcoat. The oxide coating consists of magnetic oxide particles dispersed in a polymeric binder, while the backcoat if used consists of carbon particles also dispersed in a polymeric binder.

The polymeric binders being described are those from an elastomeric (rubber) class called "polyester urethanes," which are employed either by themselves or in combination with other polymeric materials intended to achieve special properties peculiar to the tape manufacturer. There are many manufacturers of polyester urethane elastomers offering different grades which vary in mechanical and physical properties as well as in processing requirements. However, all polyester urethanes and all polyester polymers in general (Refs. 1-7) are susceptible to degradation by chemical reaction with water, a chemical reaction called "hydrolysis."

Commercial, backcoated, wide-band instrumentation tapes of this construction are used in spacecraft tape recorders, usually in hermetically sealed cases with an internal relative humidity (RH) of 30 percent. During the 1970's, there was intense interest in understanding the long-term aging characteristics of these tapes, both in the hermetic spacecraft environment, and for duplicate tapes which are archivally stored during the mission lifetime. Accordingly, a study was carried out on the environmental aging of magnetic recording tape with polyester urethane binders in both air and nitrogen, at incremental levels of relative humidity between 0 and 100%, and for various temperatures up to a limit of 75°C. Aging in nitrogen was intended to investigate if tapes were sensitive to oxidation, in the range from ambient to 75°C.

EXPERIMENTAL FINDINGS

Detailed descriptions of the hydroscopic behavior of tape, hydrolysis chemistry, experimental methods, and mathematical derivation of tape aging kinetic expressions are given in Refs. 8, 9, and 10. The results from these papers can be summarized in the following key experimental. observations:

1) No sensitivity to oxidation was detected in the temperature range up to 75°C

2) Tape aging (degradation) was totally caused by reaction with atmospheric moisture (hydrolysis) and the polyester urethane binders, causing the generation of gummy and sticky by-products

3) The hydrolysis reaction was found to be a reversible chemical reaction, thus there would also be chemical equilibrium for which no aging would occur. That is, there would be conditions of temperature and humidity which could be specified for long-term chemical stability and preservation, and conditions of temperature and humidity which should be avoided.

Based on the experimental aging studies, it was possible to develop a relationship between temperature and relative humidity to specify acceptable and unacceptable environmental conditions for magnetic recording tape. This relationship is plotted in Figure 2. The shaded area is to be avoided, for exposure in this range of temperatures and humidities causes critical degradation of the polyester urethane binder. This results in the generation of excess quantities of gummy and sticky by-products which promote layer-to-layer adhesion in a wound tape pack, and stick-slip and playback errors when operated.

The results showed that tapes constructed with polyester urethane binders should not hydrolytically degrade during archival storage if a proper environment is maintained. For long-term stability and preservation of magnetic recording tape, the storage conditions should be within the clear region of Figure 2, with an optimal environment being one close to 20°C, 40 percent humidity with tight limits on fluctuations. This storage environment is close to nominal tape operating conditions and encompasses comfortable human environments.

DISCUSSION

The aging experiments described in Ref. 9 involved exposure of tape to combinations of air (2o percent 02), inert gas (N_2), humidity levels from 0 to 100 percent RH, and temperatures of 36, 48, 61, and 75°C. The key finding from the experiments is that the primary mode of tape degradation which results from atmospheric exposure involves a chemical reaction between atmospheric moisture and the polyester urethane oxide and backcoat binders. There was also no effects of oxygen, humidity, or binder hydrolysis on the magnetic oxide particles, however recent literature is reporting that iron particles used in metal particle tapes may be affected by atmospheric oxygen and humidity (Refs. 11, 12, 13), and additionally by binder hydrolysis (Refs. 14, 15).

It can be stated in summary that the primary environmental mechanism of tape deterioration by chemistry is binder breakdown from hydrolysis accelerated by temperature. From this it should be clearly recognized that up to 75°C, temperature in itself is not the degrader of tape: hydrolysis is, and temperature only accelerates hydrolysis. The products of binder breakdown are gummy, sticky materials infamous for causing tape-head stiction, layer-to-layer adhesion, increased tape drag and friction, and possibly also corrosion of iron metal particles (Refs. 14, 15) .

It is important to recognize that the hydrolysis of tapes occurs if there is access to and chemical consumption of atmospheric moisture. Any practice which isolates or limits the access of tape to humidity stops or slows hydrolysis. The study described in Ref. 9 was carried out under conditions where unwound tape pieces had maximum accessibility to atmospheric humidity; therefore the degradation rates as measured are the maximum degradation rates. It was also found that for tapes with magnetic oxide particles, any deterioration resulting from atmospheric oxygen, if it exists, is negligible compared to hydrolytic degradation of the polyester urethane binders.

The products of hydrolysis are equally as hydroscopic (water absorbent) as the parent binder, but the lower molecular weight products in combination with moisture are exceptionally adhesive (a concept which forms the basis for the adhesive industry) . Thus high humidity compounds tape problems, by generating hydrolysis products which in combination with absorbed moisture become strongly adhesive. At the very minimum, the absorbed water content of an environmentally degraded tape should be reduced before use to minimize the adhesive qualities.

It was experimentally found that the polyester urethane binder always retains a quantity of hydrolytic degradation products, the magnitude of which increases or decreases as a function of temperature and relative humidity. At constant conditions of temperature and relative humidity, the binder retains an equilibrium quantity of hydrolysis product. To cause performance problems, it was found that the quantity of hydrolyzed polyester urethane binder must equal or exceed 14 wt.% of the total binder. Brand new tapes were found to have an equilibrium content of hydrolysis products in the order of 6.7 wt.% of total binder.

In a collaborative effort (Ref. 10), a kinetic analysis of the tape's reversible chemical reaction was successfully derived, which enabled the development of a relationship between temperature and relative humidity to specify acceptable and unacceptable environmental conditions for magnetic recording tapes with polyester urethane binders. This relationship plotted in Figure 2 is a linear plot of relative humidity in percentage versus temperature, and the curving solid line in the upper right-hand corner is the relationship between RH and temperatures associated with an equilibrium level of 14 wt.% hydrolysis product in the tape. Thus exposure of tape to combinations of relative humidity and temperature in the shaded area of the upper right-hand corner will result in an eventual accumulation of hydrolysis products exceeding 14 wt.%, and therefore, performance problems from humid aging are predicted. This shaded area is defined as the unacceptable environment for sustained tape exposure or storage. On the other hand, all of the unshaded area would constitute acceptable environmental conditions. A satisfying prediction from the chemical kinetics (Ref.10) is that nominal room conditions of 20°C and 40 percent RH would result *in* an equilibrium level of 6.7 wt.% hydrolysis products. These conditions of temperature and humidity were the ambient conditions in the room where the tape of this study was stored.

A partial verification of the general validity of the conclusions drawn here comes from studies of accelerated aging performance in an Ampex study (Ref. 16). In this study tapes of three different manufacturers were exposed for a year at 55°C, 100 percent RH. Digital random sequences were recorded on these tapes, spanning low density computer to high density instrumentation application. The kinetic results predict 34 wt.% binder degradation after 30 weeks of storage for this environment. In agreement with the 14 wt.% limitation, all tapes showed serious degradation by shedding sufficiently gummy products to disallow tape transport operation after 6 to 9 months storage. Increased error rates were measured after an initial three months storage period. The chemical kinetics predict that only one month storage is required to achieve 14 wt.% binder degradation which is the anticipated onset of poor machine performance. Other tapes in the Ampex study were stored at room environments of 40 percent RH, 15°C and only a slight, almost negligible, error rate increase was measured over the study period.

From the experiments discussed above, it appears that measurements of hydrolysis upon one particular brand of tape with polyester urethane binders may be applied in general to infer storage conditions for other production tapes with polyester urethane binders. Perhaps even though tape binder systems are complicated with multitude of additives, the end product requirements result in great similarity with respect to hydrolytic behavior of tapes from different. manufacturers.

It has been common practice in the tape industry to qualify tapes for environmental stability by looking at the effect on performance, error rate, RF output, etc., from storage in an adverse environment, typically 90 percent humidity, 35°C, for perhaps a month. Even though such a test may or may not yield serious performance degradation, it is clear from this study that such a test does not relate simply to storage at room environments. An accelerated test can easily cause serious hydrolysis and poor tape performance and still the tape can be stored acceptably for many years at room temperatures at nominal humidities according to Figure 2. The principle value of such qualification tests might be perhaps to disqualify particularly bad tapes for other reasons. The best solution of course, is to understand the various chemical processes in the tape system which leads to degradation, including hydrolysis, so that a reasonable long-term storage environment can be predicted. This is particularly important since magnetic tape is always evolving and future products may not have the same chemical constituents as those being described.

This paper describes the hydrolysis of tape binder systems with regard to proper archival storage. As discussed in Reference 16, there are also mechanical considerations for optimum storage which should be considered in addition to hydrolysis in order to properly specify storage environments. Since Figure 2 can be used as a storage environment guide, it is necessary to include briefly the mechanical consideration from Reference 16.

The essential mechanical considerations are 1) storage at high temperatures increases the stress relaxation of the pack, 2) increase of temperature above the winding temperature increases the pack pressure due to differential expansion of the pack and hub, and 3) a decrease in storage humidity below the winding humidity can lead to increased pack pressure due to hydroscopic contraction of the pack relative to the hub. These three factors can lead to pack slip or cinching once the tape has been returned to operating environment and thus to increased rewind frequency requirement. Given these mechanical considerations, it is suggested that in preparation for long-term storage, a wound pack of tape be temporarily stored a minimum of three days in the same temperature and humidity environment as the long-term storage environment., to achieve temperature and humidity equilibrium. Following this brief period, the tape should then be wound onto the reel intended for long-term storage. Given the chemical consideration that error rates will increase if hydrolysis occurs, a most reasonable winding and storage environment should be near 20°C, 40 percent RH with tight limits in fluctuation to reduce rewind frequency.

RECOVERY OF DEGRADED TAPES

High Humidity. The experimental studies described in Ref. 9 and 10 found that tape hydrolysis can be reversed, offering the possibilities of rejuvenating environmentally degraded tape, but it is important to emphasize that rejuvenation times can be impractically long. For example, suppose a tape is inadvertently degraded from three months of exposure to an environment of 100 percent RH and 35°C (e.g. , a summer) . If it is desired thereafter to restore the tape to the original chemical condition by storage at O percent humidity and 35°C, 27 weeks of rejuvenation time would be required. Restoration times are generally long, as this example indicates. As a practical matter, it has been shown (Ref. 16) that 1-3 days storage in a room environment (i.e., 20°C, 40% RH) followed by perhaps a tissue wipe is sufficient to return the tape to a playable low-error-rate state. The former is the time required for hygroscopic diffusion to remove water (Ref. 8), and the latter to remove gummy surface debris left from the hydrolysis process (Ref. 9). If the degraded tapes are still not playable, a heating treatment described in the next section may be considered.

Liquid Water. It is to be observed in Figure 2 that at 100% relative humidity, or liquid water, temperatures less than 11°C (53°F) does not cause critical hydrolysis. If tapes are submerged in water, as caused by a flood, or accidentally dropped in oceans or lakes, the temperature of the water at the location of the tapes should be determined. If the water temperature is less than 11°C, the tapes should not be degraded and therefore easily recoverable. If the water temperature is greater than 11°C, the tapes may or may not be recoverable, and which will have to be assessed on an individual basis.

On recovering the wet tapes, they should be immediately placed in ice-water at nominally 0*C. This keeps the tapes wet, causes no harm, and stops hydrolysis if the tapes were in water warmer than 11°C. The tapes can be gently moved in the ice-water to rinse away any surface dirt, sand, or other solid matter. Following this, the clean tapes should be transferred to a fresh ice-water bath.

At this point, a careful inspection can be optionally carried out to determine the ease or difficulty of unwinding the wet tape. This can provide an early clue about the level of degradation. Do not attempt a vigorous effort to unwind the tape, as this may cause permanent damage to the oxide coating, or oxide shed. Be aware that the wet tape pack may be under considerable tension from hydroscopic expansion of the tape layers, and that also any water, water-borne debris, and/or sticky binder hydrolysis products in between the tape layers could be causing tape cling, or layer-to-layer adhesion which will resist unwinding.

If the tapes can be easily unwound while wet, it is recommended to transfer the tape loosely onto another reel, preferably in ice-water to rinse the layers as they become unwound, or in a cold room having a temperature less than 11°C.

Transfer the wet tapes into a vacuum chamber for dry-out. This chamber may be identical to those already used in libraries for drying out wet books or other wet documents. Do not heat the tapes. It is recommended as a cautionary procedure to slowly dry the tapes, and for guidance, it is known (Ref. 8) that under hard vacuum, 17.4 mm tapes require two to three days for total dry-out, and 25.4 mm tapes require four to five days.

After vacuum dry-out, expose the tapes to an ambient environment of 20 to 25°C and 30 to 50% RH. Again (Ref. 8), wound packs of 17.4 mm tape will require two to three days for moisture regain, and 25.4 mm tapes will require four to five days. Do not attempt to unwind dry tape, as in this state, the tape may be brittle.

After moisture regain, an effort to carefully unwind the tapes should be attempted. Tapes which were exposed to cold water (<11° C), or moderately degraded tapes, should unwind with reasonable force which does not cause mechanical damage to or shedding of the oxide coating. If the tapes can be unwound, a tissue wipe of the tape on a standard tape cleaner is advised before attempting playback of the tape. Maintain a room humidity in the range of 30 to 50% RH when tissue-cleaning the tape, and during playback.

At this stage of the recovery procedure, there may be two situations which could occur for severely degraded tapes. The first is that the tapes can be unwound and wound from reel-to-reel, but cannot be played without squeal, stick-slip, high error rates, gummy and sticky deposits, shedding of oxide, and so on. The second is that the tape pack cannot be unwound at all, without oxide damage.

To achieve a playable condition, a high risk procedure can be attempted. This procedure involves heating the tape pack at 75°C, in vacuum or in dry nitrogen, in an attempt to chemically reverse the hydrolysis reaction, to restore the binder chemistry and its mechanical and physical properties, and to reduce the quantity of hydrolyzed products in the polyester urethane binders. The rate of restoration chemistry is very slow, and many weeks may be required. There is a reasonable chance that a playable state may be achieved for tapes which could be unwound and wound prior to this heating procedures, and a very low chance for very severely degraded tapes which could not be unwound prior to the heating procedure. Attempting the procedure is a risk/reward trade-off decision, and the heating procedure may have to be repeated several times. Be reminded that after each heating cycle, the tape must be re-equilibrated to 20 to 25°C and 30 to 50% RH, before attempting to unwind, clean, or play the tape.

CONCLUSION

The results of an experimental study of the hydrolysis of a magnetic recording tape containing magnetic oxide particles and polyester urethane binders has been described. It is found that the hydrolysis reaction is reversible, thus definite environments exist which permit long-term archival storage of the media, Although the data utilized in the study involved one tape used for spacecraft applications, the general findings were supported from long-term aging of tapes from three different manufacturers stored under hydrolyzing environments at 55°C and 100% RH. For these tapes, the aging resulted in the generation of excess quantities of gummy and sticky by-products which promoted layer-to-layer adhesion in a wound tape pack, and stick-slip and play back errors when operated.

The results of this study suggest that tapes constructed with polyester urethane binder systems should not chemically degrade during archival storage if a proper environment is maintained. For long-term stability and preservation of magnetic recording tape, the storage conditions should be within the clear region of Figure 2, with an optimal environment being one close to 20°C, 40% RH with tight limits on fluctuations. This storage environment is close to nominal tape operating conditions and encompasses comfortable human environments.

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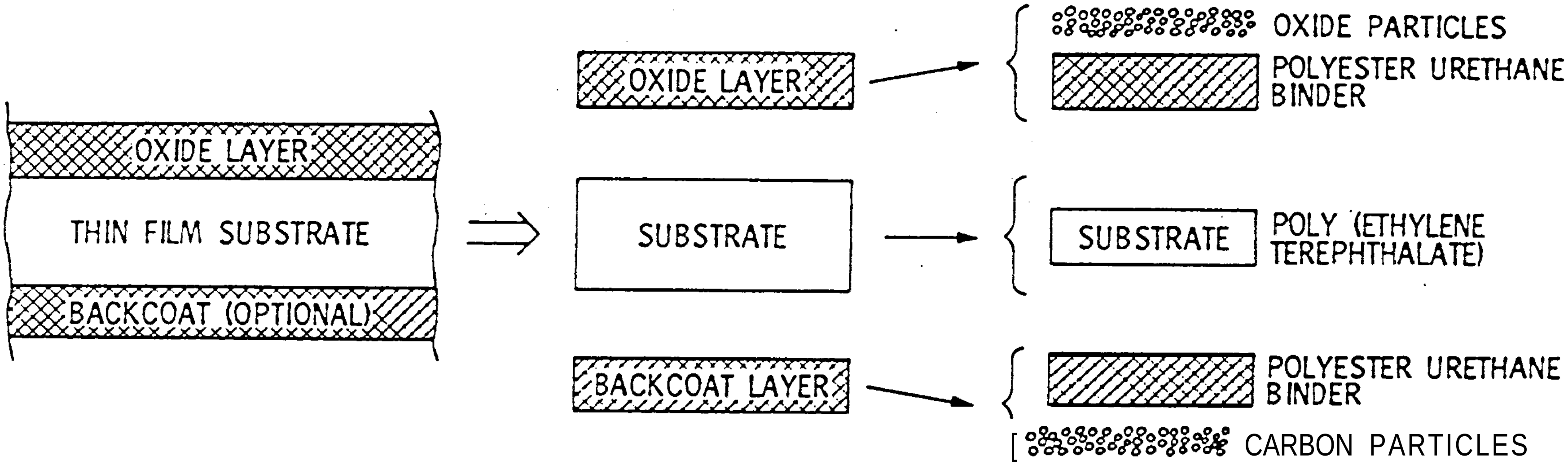
FIGURE TITLES

1) Basic Components of Magnetic Recording Tape with Magnetic Oxide Particles and Polyester Urethane Binders

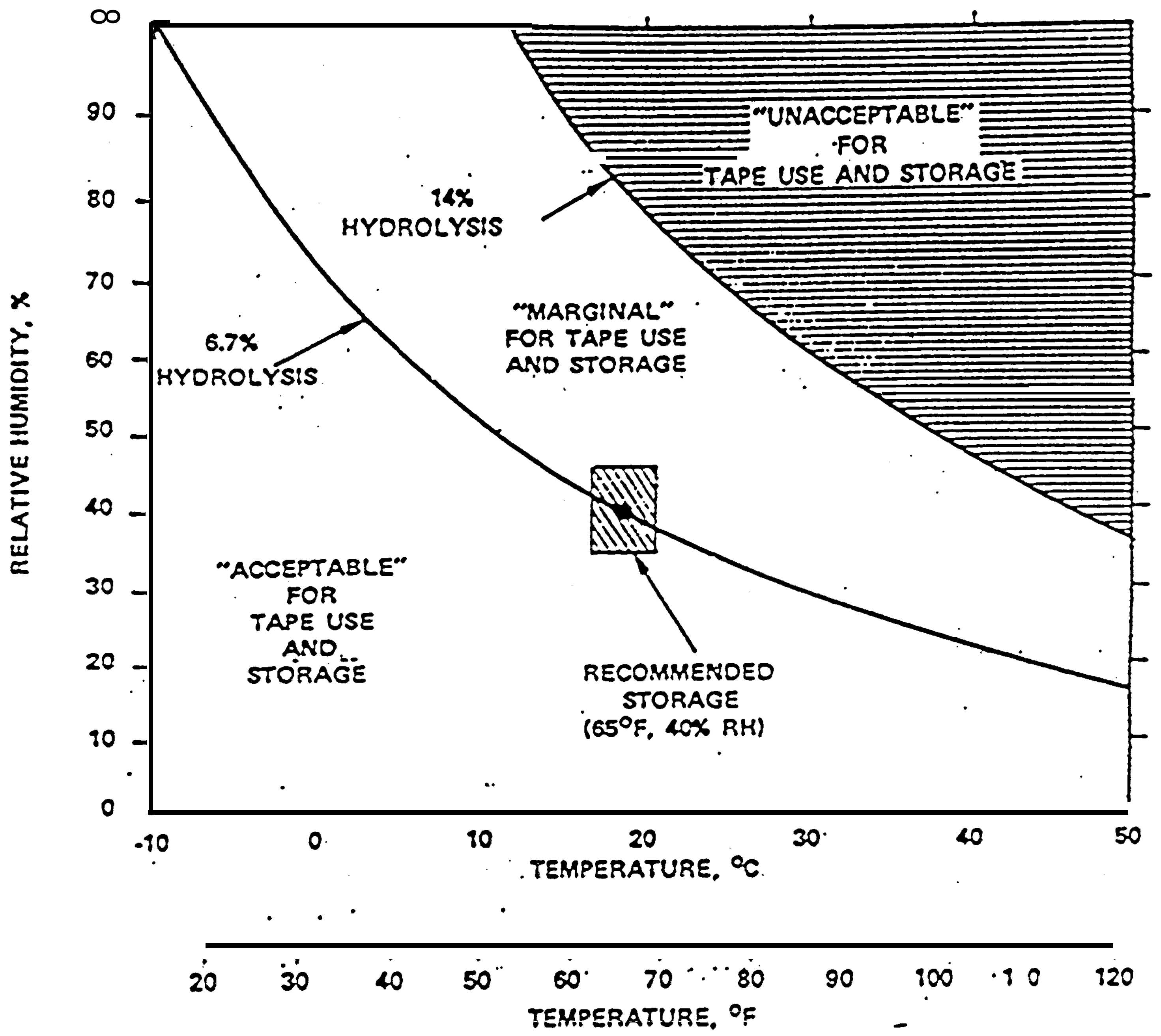
2) Acceptable and Unacceptable Ambient Environments for Unprotected Tape Use and Storage

FIGURE 1.



COMPOSITION: 20 wt. % MAGNETIC OXIDE PARTICLES
80 wt. % POLYMERIC MATERIALS

FIGURE 2.


∞
90
80
70
60
50
40
30
20
10
0
RELATIVE HUMIDITY, %
"UNACCEPTABLE" FOR TAPE USE AND STORAGE
14% HYDROLYSIS
"MARGINAL" FOR TAPE USE AND STORAGE
6.7% HYDROLYSIS
"ACCEPTABLE" FOR TAPE USE AND STORAGE
RECOMMENDED STORAGE (65°F, 40% RH)
-10
0
10
20
30
40
50
TEMPERATURE, °C
20
30
40
50
60
70
80
90
100
1 0
120
TEMPERATURE, °F