



Audio Engineering Society Convention Paper

Presented at the 139th Convention
2015 October 29–November 1 New York, USA

This Convention paper was selected based on a submitted abstract and 750-word precis that have been peer reviewed by at least two qualified anonymous reviewers. The complete manuscript was not peer reviewed. This convention paper has been reproduced from the author's advance manuscript without editing, corrections, or consideration by the Review Board. The AES takes no responsibility for the contents. Additional papers may be obtained by sending request and remittance to Audio Engineering Society, 60 East 42nd Street, New York, New York 10165-2520, USA; also see www.aes.org. All rights reserved. Reproduction of this paper, or any portion thereof, is not permitted without direct permission from the Journal of the Audio Engineering Society.

Some Observations On Vinegar Syndrome

Scott Dorsey¹

¹*Kludge Audio, Williamsburg, VA, USA*

Correspondence should be addressed to Scott Dorsey-Author (kludge@panix.com)

ABSTRACT

In the 1980s it became evident that cellulose triacetate, used as a base for motion picture film and recording tape, was unstable and occasionally suffered from deacetylation with no clear pattern as to which material would be stable and which would not. The author recaps existing research on the nature and basic chemistry of vinegar syndrome, adding some observations of his own on various triggers, and describes a unsuccessful attempt to replasticize damaged film and tape so as to make it playable.

1. INTRODUCTION

For several decades now, vinegar syndrome has been known to exist in various archives. Similar problems appear to affect both motion picture films and acetate-based audio tapes, but the source of the problem appeared to be a mystery for a long time because it was (and remains) impossible to predict which materials will be affected.

Although it is clear that storage conditions have much to do in starting this process, two tapes recorded at the same time, from the same batch of tape, stored in the same way, may be affected differently with one tape degrading completely and the other seeming to be untouched.

Early on, it became clear that the nature of the prob-

lem was deacetylation of the acetate base material, causing acetic acid to be split off. This acetic acid resulted in lower pH of the base material which itself accelerated the deacetylation. This positive feedback effect meant that once the process started in a sealed film can, it would accelerate at a rapid pace.

This acceleration in part was responsible for the dramatic differences between materials, since whatever triggered the process would cause fairly rapid breakdown.

Early on it became clear that the better vented the material was, the slower this process would progress, and consequently it seemed to be less of an issue in open cardboard tape boxes compared with sealed film cans.

Processed film seemed to be affected in a random way, with the problems not affected by a given lab's washing or processing procedures.

It appears that iron oxide coatings make the process more likely to be started; some facilities used scrap magnetic film as leader for picture films and this was found to increase the likelihood of vinegar starting. There has been a perception in the industry that film stored on steel reels also is more likely to suffer than film on aluminum or plastic reels although the author knows of no statistical verification for it.

Very importantly, it was found that early diacetate films which were less completely acetylated in the first place did not suffer from this breakdown process.

2. INITIATION OF BREAKDOWN

Again, because this process is autocatalyzed, once the process begins it accelerates, so only a very small difference in storage conditions at one point in the life of a medium may result in very different end results.

When it first became clear that there was some undefined sort of deacetylation taking place, N.S. Allen and others [1] performed a short study in which they created acidic conditions on test films in the laboratory and analyzed the accelerated breakdown process.

They determined that relative humidity in storage conditions had a dramatic effect on the process but curiously very high humidity conditions can dilute the acid and slow buildup. They found that the thicker emulsion applied to positive films has some protective effect and that the action of the plasticizer appears to slow the process (presumably because the breakdown of the plasticizer creates alkaline breakdown products).

In any event, it has become very clear that acetate films can last a long time in cold storage but that storage conditions are critical to keeping film and tape stabilized [2]. Once the process begins it is difficult to slow or stop.

3. CAUSES

In 1992, Shinagawa [3] hypothesized that the original breakdown mechanism is the result of the action

of triphenyl phosphate used as a plasticizer in the original material. His argument was that under acid conditions, TPP breaks down into diphenyl phosphate which catastrophically lowers the pH leading to the acetyl groups breaking off of the cellulose chain.

Although this mechanism appears not to be the case, since further research by McGrath [4] failed to find evidence of DPP residue, it does appear that TPP is implicated in the breakdown process.

Evidence in its favor include McGrath's investigation finding that in degraded plastic of acetate aircraft models that deacylation was more significant in areas with higher TPP concentration, and the lack of breakdown of the diacetate materials which were softer and did not require an added plasticizer.

4. IMPLICATION OF IRON

It has been "common knowledge" among archivists that films with magnetic coatings or stripes are more likely to be affected, and that films stored on "old and rusty" steel reels are more likely to be affected. Although "common knowledge" is often wrong, there is a lot of anecdotal evidence to support this.

Although no studies on film and tape appear to have been conducted, there have been some studies on acetate reverse-osmosis membranes which show deacetylation caused by a strong oxidizer can be catalyzed by salts of various 3d transition metals including iron [5].

This is one of the points where additional study is most needed, both in more thoroughly verifying the existence of the problem and knowing the mechanism involved which may help us find a way to interrupt or slow it.

In the meantime it is recommended that film not be stored on steel reels and in steel cans. Unfortunately there is nothing to be done to prevent contact between iron oxide and the acetate base for magnetic materials.

5. BASE COMPOSITION

The assumption is made here that the base consists entirely of acetylated cellulose and a plasticizer, whatever solvent having been used in preparation

having evaporated. To verify this and to assure that the standard plasticizer package originally used for film materials was simply TPP, a brief patent search was conducted.

The basic rosetta stone as far as opening up the composition and manufacture of acetate film base material is the original 1946 Kodak patent[6]. This patent describes a method for evaporation of a highly acetylated cellulose polymer along with triphenyl phosphate and mentions no other plasticizers being used. It does not mention any pH buffering as part of the process.

Another Kodak patent, 51 years later[7] describes a modernized and improved version of the same process. By 1997, the plasticizers available include triphenyl phosphate, dibutyl phthalate, tricresyl phosphate, butyl stearate, and tetraethylene glycol dimethyl ether. The author's assumption is that any material described in a patent is going to be one in common use and so there may be trade secret materials also in use. Consequently, this list of plasticizers describes everything in common use in 1997 and hopefully any trade secret item from 1946 should be in common use by 1997.

A 2000 US patent from Daicel Japan[8] describes an extensive and far wider range of plasticizers, including triphenyl phosphate, tricresyl phosphate, dimethyl phthalate, diethyl phthalate, diethyl phthalate, dibutyl phthalate, dioctyl phthalate, diethylhexyl phthalate, O-acetylcitric acid triethyl ester, and O-acetylcitric acid tributyl ester. Also butyl oleate, acetylricinoleic acid methyl ester, dibutyl sebacate, and trimetallates. This seems to provide a complete list of all plasticizers ever even considered for use with acetate films. The authors state a preference for phthalate plasticizers but that may apply only to their particular formulation.

6. A REMEDY?

Over the years attempts to rewash or alkalize films have been unsuccessful; use of a mild alkali solution just strips additional acetyl groups off once the deacetylation process has begun, and the deacetylated base is hydroscopic which makes the use of any aqueous solutions problematic.

Several companies have sold products which are claimed to halt or cure vinegar syndrome, most notably **VitaFilm** by Stewart Motion Picture Services.

None of these products have been tested and attempts to obtain material safety data sheets or any documentation on what they might contain have been unsuccessful.

In 2012, Nadja Wallaskovits from the Austrian Academy of Science gave a talk at an AES conference in which she discussed various difficulties with older historical magnetic tape. [9]. She mentioned almost in passing that they had a process there at the Vienna Phonogrammarchiv to restore acetate materials by replasticizing them and normalizing the pH. Although no details were given, in questions after the presentation she explained that it involved treating the materials with the original plasticizers used in their manufacture. She specifically used the plural form, "plasticizers" and when asked about whether a solvent used, claimed that none was employed.

This author, therefore, made the assumption that this is probably a mixture of triphenyl phosphate and some other liquid plasticizer, possibly tricresyl phosphate, as these were most likely candidates for earlier acetate materials. Alternately, it was felt possible that it could have been a weak solvent combined with one of these two plasticizers. Consequently, a brief set of experiments was made to determine whether this was the case.

7. SOME TESTS

In an attempt to figure out what was going on, the author performed several simple tests where severely degraded film was soaked in plasticizer/solvent mixes over a three-week period. A description of the results in each of these tests is provided.

7.1. 1:1:3 acetone, glycerol, and water alone

After one week, film is softened but still shrunken. Extremely fragile and rubbery, can be pulled apart with fingers. After three weeks film is softer but remains extremely curled.

7.2. Saturated solution of TPP in naphtha

No change after one week. This is the least effective of the set; little TPP went into solution and the naphtha did not appear to penetrate the film base. No change after three weeks.

7.3. Saturated solution of TPP in isopropanol

After one week film was softened in solution but returned to original state when the film was dried. No

additional change after three weeks. Clearly the isopropanol is penetrating the film base but TPP is not.

7.4. Saturated solution of TPP in 1:1:3 acetone, glycerol, and water

Identical to same solution without TPP.

7.5. Saturated solution of TPP in TCP

No evident change after one week. No evident change after three weeks.

7.6. Pure TCP

No evident change after one week. No evident change after three weeks. It appears the high molecular weight of the TCP is preventing it from being absorbed into the base at all.

7.7. Discussion

It can be seen from this that in some cases solvent penetration of the base was very good, in other cases it was very poor, but in no case was the absorption of plasticizer sufficient to improve film flexibility appreciably except in the simple case of water/glycerol/acetone, and in that case although flexibility was improved the film remained shrunken and fragile.

It is entirely possible that the film tested with was too degraded for the process to work on; the most degraded film available was used for testing. It is also entirely possible that the solvent has penetrated the acetate but that the much larger molecules of the plasticizers are not being carried into the plastic to sit between the chains of the polymer. If this is the case, perhaps treatment under much higher than atmospheric pressure, or at higher temperatures would be more effective. On the other hand, since it is clear that polar molecules like water penetrate well, and nonpolar materials like naphtha do not, that the nonpolar nature of both triphenyl phosphate and tricresol phosphate[?] is responsible for the poor absorption in spite of the solvent and that increased temperature or pressure would be of little aid.

The author can state that the Vienna Phonogram-marchiv process does in fact exist and he has seen material shipped off for processing in poor condition and usable film returned. However, he is unable to

make any good argument for how the process operates. It is clear that there is a need for a skilled plastics chemist to investigate this problem.

8. CONCLUSION

The process of deacetylation and some of the basic mechanism has been described as well as some of the factors that go into causing it. An existing proprietary process has been mentioned and some attempts made to determine how it operates but without success.

9. REFERENCES

- [1] Allen, N.S. et al, *Acid-Catalyzed Degradation of Historic Cellulose Triacetate, Cinematographic Film: Influence of Various Film Parameters*, Eur. Polym. J. Vol 24, No. 8, pp. 702-712, 1988.
- [2] ANSI, *American National Standard for Imaging Materials— Processed Safety Photographic Films— Storage*, PIMA IT9.11-1997, New York: American National Standard Institute, 1997.
- [3] Shinagawa, Y., Murayama, M. Sakaino, Y. et al., 1992. Investigation of the Archival Stability of Cellulose Triacetate Film: The affect of Additives to CTA Support. N.S. Allen, M. Edge and C.V. Horie, eds. *Polymers in Conservation*, 105, pp. 138-150.
- [4] McGrath, M.K., *Investigation of Deterioration Mechanisms of Cellulose Acetate Compounded with Triphenyl Phosphate*, dissertation, University of Arizona 2012.
- [5] Murphy, Andrew P., *Accelerated deacetylation of cellulose acetate by metal salts with aqueous chlorine*, Research Journal WPCF, Vol 62, No. 2, March/April 1991.
- [6] Eastman Kodak Corporation, US patent 2,492,977, 1946.
- [7] Eastman Kodak Corporation, US patent 5,686,036, 1997.
- [8] Daicel Japan, US patent 6,139,785, 2000.
- [9] Wallaskovits, Nadja, *The Replay of Historical Magnetic Tape— More Than Pressing The*

Play Button. Historical program presentation H5, presented at the AES 133rd convention, San Francisco, CA, 2012 Oct 26-29.

- [10] Barton, Allan F.M., *Handbook of Solubility Parameters and Other cohesion Parameters*, ISBN 0-8493-0176-9, CRC Press, 1991.