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Basic Tape Chemistry

ABSTRACT

A basic survey of chemistry of magnetic tape over the course of the past eighty years, introducing the changes over time in binder, base, and magnetic pigment formulations. A bibliography, references, and various pointers to more information available publicly are provided.

1 Introduction

I have recently been seeing a lot of misinformation about tape manufacture and tape chemistry, as well as a lot of people claiming that all of the information about tape formulations are proprietary and that therefore nobody can possibly know anything about what went into the original tapes. Although much information is proprietary there is also a lot of information about tape formulation and manufacture in the open literature and this paper is a brief attempt to compile pointers to that information in a single place.

A good basic description of the physical process of tape manufacture as noted in reference[1] may be of help to understand the overall requirements.

I have included some surmises and guesswork about why changes were made. There was a great push to increase audio tape output levels, and this was done primarily in four ways: thicker coatings, higher pigment loading (ie. more pigment in the binder), better control of particle size and shape, and better control of particle alignment in manufacture. The first two of these greatly affected physical chemistry of the material.

The initial patent for magnetic tape recording can be found in reference [-1] but contains no details about how to manufacture an effective medium.

2 Base

The tape base provides a tough support to hold the oxide layer in place. Various materials for the base have been used over the years, of varying stability.

2.1 Paper

Paper-based tape was made by 3M before the war for use with voice-grade recorders. A similar tape was manufactured by Gevaert in Germany. These tapes are very rare but survive well. Archivists have a good understanding of techniques for preserving paper.

A major advantage to paper base is that there is good adhesion to paper with just about any binder chemistry, even simple PVA or nitrocellulose lacquer.

These tapes can be easily identified by the thick white or brown base and the fibrous material seen when the end is torn.

A good introduction to the basic process mechanically can be found in reference [0], although there is no discussion of the precise type of paper or the binder used. A good general reference to the chemistry of paper can be found in reference [0.5].

2.2 Triacetate

Cellulose Triacetate is a trade name for a fully-acetylated cellulose polymer. It was initially invented by Eastman Kodak and complete details on a typical formulation may be found in a Kodak patent[4.2]. By the time 3M was looking at magnetic tapes it was a material with a fairly well-established track record.

Pure cellulose was reacted with acetic anhydride in a solution. By fully acetylated, we mean that all of the hydroxyl groups on the cellulose chain were replaced with acetyl groups. This resulted in a hard and stiff but rugged material. You can think of it as long chains of cellulose rings with acetyl groups hanging off each one.

In order to make the material more flexible for use as a tape base, a plasticizer was used. Initially triphenyl phosphate and tricresyl phosphate were used, but later on phthalates and a number of other compounds were used as well. You can think of these as small, almost spherical molecules that lie between the long cellulose molecules and act as ball bearings to permit them to slip back and forth next to one another, improving flexibility.

The mix of acetylated cellulose, plasticizer, and solvent would be spread on the top of a huge, slowly rotating wheel with a chromed surface, and as the wheel turned the solvent would be evaporated off and the finished material peeled away from the wheel. This process was initially invented by Kodak [2] but was extensively licensed. Additional details can be seen in a later Kodak patent [2.1].

The primary known failure mode of these tapes is a reaction between the cellulose acetate and the triphenyl phosphate causing deacetylation of the tape. Acetyl groups break off and form acetic acid, and as the tape pH drops the reaction progressively speeds up[3]. This is known by archivists as “vinegar syndrome.”

It seems that iron oxides can help initiate this process, as has been found by comparing cine film from the same manufacturing process with and without oxide sound stripes, and by observing that film on iron reels is much more apt to go vinegar than film on plastic or aluminum reels. Additional evidence can be found in [4].

Films and tapes plasticized with other plasticizers such as tricresyl phosphate or phthalates do not seem to be subject to vinegar syndrome breakdown.

Acetate tape can be easily identified by the extreme flexibility of the tape compared with other bases, and by the ease of breaking when torn against the long direction of the tape.

2.3 Diacetate

“Cellulose diacetate” which is to say a cellulose which was not completely acetylated, was briefly used for home movie films before the availability of triacetate. This material does not suffer from vinegar syndrome since it is flexible enough to be used without plasticizer, but mechanical properties are poor. It was, however, used by Audio Devices for some tapes[5]. Appearance of the final tape is similar to that of triacetate.

Details on the manufacture of this material can be found in the original Kodak patent of 1926[4.1].

2.4 Polyester

The polyester film used for magnetic tape is biaxially-oriented polyethylene terephthalate, often referred to by the tradename “Mylar.” This is a stretched PET film with extremely good dimensional stability and longevity.

In manufacture, molten PET is extruded onto a chill roller much like manufacturer of acetate films, but it is then drawn out on heated rollers and reheated which prevents it from shrinking back to the original shape and orients molecules parallel to the direction of travel. The process, including details of chemical composition as well as the orientation process, can be found in the original DuPont patent of [4.3].

PET is extremely stable. When stretched, it will form curled “spaghetti” long before breaking. PET film was first used for audio tapes by Reeves Soundcraft in 1952[6].

In 1976, chemists at 3M patented a nonuniform base in which polyester film was manufactured with embedded nylon, styrene, or other compatible polymer particles[23]. This allows creation of a microscopically irregular back tape surface without the need for back-coating. This was used in some 3M computer tapes but has not been seen in audio materials.

Adhesion to mylar bases is more problematic than acetate, so the change to mylar resulted in some changes to the binder chemistries as a result.

2.5 PVC

Some wartime I.G. Farben tapes used polyvinyl chloride bases but 3M did not adopt this after the war. However in the 1970s there were some inexpensive tapes made in Japan using PVC, imported into the US for consumer applications. These are rare but very delicate, and the only one I have encountered was sold by Sun-Mark of Danbury, CT. There were also some PVC-based tapes made in the late 1950s by Agfa.

A 1960 survey in the UK of various available tapes came up with two German tapes of undisclosed manufacture with PVC bases[19].

PVC is a thermoplastic polymer, it is very stiff, and like triacetate has to be mixed with a plasticizer to make it flexible. Which plasticizers were used in the German and Japanese tapes is not known.

These tapes are distinguished by their fragility. Right off the production line they were so delicate that they would tear if twisted. Evaporation and loss of plasticizer causes these tapes to become hard and brittle.

3 Binder

The binder is the adhesive used to keep the pigment in place on the tape. Various binder chemistries have been used over the years for different applications. For example, a computer tape or video tape might need a very durable coating to withstand multiple high speed head passes, while an audio tape may need a binder that can handle a very high pigment load to get the highest possible output.

The binder chemistry has changed dramatically since recording tape was first introduced. These changes are for the following reasons:

- Changes in the base material. Early latex-based binders would adhere well to acetate but not so well to polyester
- Increases in production speed. Binders that rely upon evaporation of solvents to set moved to more volatile solvents and thermosetting materials that would set more quickly were introduced.
- Demands for greater ruggedness. The videotape and computer fields required very rugged binders and as these technologies were developed they moved into audio tapes as well. Multitrack recording with many progressive passes began to make a need for rugged binders in the audio world too.
- Demands for higher output, and one of the ways to get this is with a thicker coating and a higher pigment load in the coating.

I mention here only a few well-documented binder chemistries. Mee and Daniels also mentions the use of the following: polyvinyl formal, polyvinyl acetate resins, acrylate and methacrylate resins, combinations of polyether with OH groups with polyesters and polyvinyl chloride, modified cellulose derivatives, epoxy and phenoxy resins, and polyamides[13].

An excellent overview on how the various components of the tape coating interact (including discussion on binder-to-pigment ratios) can be found in reference [33].

Some interesting photos of the original coating line at Orr Radio in 1955 can be found in reference [34], showing just how small scale early operations were.

3.1 Nitrocellulose

Nitrocellulose lacquer was used in some older tapes and magnetic films, and was initially promoted for use in striping motion picture films[36]. This paper describes a formulation involving nitrocellulose, maleic resin (modified wood rosin), solvents, and castor oil as a plasticizer. This is quite similar to lacquer paints and to lacquer used as film cement, and adheres very well to acetate and paper (but not at all to mylar).

A similar formulation is given in [37] using only nitrocellulose, castor oil, and solvents, with no reinforcing maleic resin.

3.2 PVA/PVC

Until about 1960, most tape binders were polyvinyl plastics such as Saran[14]. These are fully thermoplastic. Later developments produced binders able to produce smoother tape surfaces, maintain a more even oxide dispersion, and produce better wear characteristics, but even so the PVC and PVA compounds remained in use at least until 2005.

A 1960 survey and analysis of various tapes showed the majority tested used a vinyl chloride/vinyl acetate, carboxylated vinyl chloride, or chlorosulfonated vinyl chloride polymer binder[19].

PVA/PVC doesn't stick very well to mylar, so this was presumably one of the major reasons for newer binder formulations

Ampex 641 is a typical example of a tape employing this binder chemistry.

A typical coating line employing binder with chemistry like this can be seen in reference [39]. The system shown appears to reflect current technology as of 1956 and employs a thin adhesive layer applied to the base before laying down the magnetic coating, although the chemistry of neither the adhesive layer nor the coating are discussed.

3.3 Thermoplastic Urethane

Polyurethanes are a whole family of polymers of generic organic units that are jointed by urethane (carbamate) groups. They are formed by reacting an isocyanate with a polyol. The individual monomers are bound together in such a way that they form a zig-zag, which is responsible for the flexibility of these compounds. A good introduction to the chemistry of urethane coatings can be found in reference [15].

Polymer chemists use the word "polyol" to describe any compound with multiple hydroxyl groups available. The same word is used differently by food chemists which can result in confusion. A wide variety of possible polyols exist for manufacturing urethanes, among them the popular polyesters. These are often referred to in the literature as "polyester urethanes" when in fact they are polyester precursors to urethanes and not yet urethanes themselves.

"Polyester Urethane" or PE-PE is also used to refer to a copolymer involving soft segments of polyester oligomers of adipic acid, along with hard segments of short polurethanes made from 4,4'-diphenylmethane diisocyanate bonded together[51]. The Estane family of polymers are typical.

By 1966, urethane binders were increasingly in use in newer tape formulations[14], presumably mostly for non-audio applications where ruggedness was critical.

The initial patents describe simple polymers but in actual use nitrocellulose may be added as a modifier to

increase tensile strength of softer resins. It is also possible to compound urethane binders with other resins to form copolymers with better characteristics (as described in sections below).

The initial patent describing the use of urethane binders is Herbert Bauer's 1961 patent from RCA[18]. This patent has a very good description of the chemistry involved, using Adiprene L100 and L167 polymers from DuPont combined with 4-4'-methylene dianiline as a polymerizing agent as well as some RCA-made resins. This binder was designed for computer tapes where ruggedness is paramount but does not appear to have been used extensively.

This is interesting in that this is neither completely thermosetting nor completely thermoplastic. The coating is mixed up and begins to polymerize in the vat, but is kept in solution by the solvent. However, the polymerization continues after the coating process and some additional curing is still required.

It should be pointed out here that insufficient levels of the curing agent in such a formulation will result in poor long-term stability.

3.4 Urethane/PVA/PVC

In 1962, Masaki Morita and others from Sony patented a binder which was a mix of a urethane with a PVA/PVC copolymer, claiming better heat and abrasion resistance over a simple PVA/PVC binder.

Their example formula mixed a metallic pigment with an undescribed plasticizer, an undescribed polyester resin, and a PVC/PVA copolymer (once again Union Carbide VAGH), along with a solvent, stabilizer, and lubricant. Then an isocyanate was added to react with the polyester resin to form a polyurethane and it was coated and then cured at 50deg to 70deg C for 24 hours[27]. A later discussion of VAGH can be found in reference [16].

Similar copolymers were known to have been used in many consumer tapes. Mr. Morita, decades later, retired as president of Sony.

A completely thermoplastic urethane PVA/PVC coating came from Karez in 1972. The arguments made in the patent [30] are that thermoplastics have an indefinite pot life, curing is a non-issue, and chemical interactions with the pigment are minimal. Therefore the authors considered development of thermoplastic

binders, even as late as 1972, to be worthwhile. They present a formula using VYNS vinyl resin from the Bakelite company, and a thermoplastic polyurethane-polyurea resin from Goodyear chemical such as TPU 123, TPU 546, or TPU 552, along with a pigment, lubricant, lecithin, carbon black, and a solvent. That is, the polymerization is done entirely at the Goodyear factory and the pre-polymerized material is added into the coating mix.

This binder does not seem to be significantly different in terms of final composition than the earlier Sony copolymer and similar compounds are likely to have been used elsewhere before and after the time of this patent.

Composition of an improved urethane resin for use in such binder formulations can be seen in a much later 1991 patent from B.F. Goodrich[29]. This chemistry likely arrived too late to have been applied anywhere. However the patent shows various formulations using the new resin, comparing them with older formulations using Estane 5701 and as such the patent is useful as a reference of those older existing formulations.

3.5 Urethane/Vinylidene Chloride/Acrylonitrile Copolymer

In 1964, Ampex patented a binder utilizing a mixture of a urethane such as B.F. Goodrich's Estane X-1 or X-2, with a vinylidene chloride/acrylonitrile copolymer such as Saran F220 used in the example[20]. This again is employing a pre-made urethane with all the polymerization done by Goodyear, with the vinyl mixed in and no additional agents added, so the curing process is likely entirely simply evaporation of the solvent.

This again was intended for computer tapes to improve ruggedness. It is not known if this binder was actively used for audio tapes.

3.6 Urethane/Phenoxy Binder

In 1967, Ampex patented a similar copolymer arrangement with a polyurethane resin made harder and more durable with the addition of an epoxy resin[22].

In one case, they create a thermoplastic mixture of a phenoxy resin (such as Union Carbide's PRDA-8080) and an elastomeric polyurethane resin (such as the Estane X-1 or X-2), and a solvent.

The patent mentions also possible addition of carbon black for static control, fungicides such as phenyl mercuric oleate, dispersants such as lecithin and lubricants such as silicones.

3.7 Urethane/Phenoxy/Phenolic Resin

The aforementioned 1967 patent[22] also includes a formula for a thermosetting system.

In this case, they create a thermoplastic mixture of a phenoxy resin (such as Union Carbide's PRDA-8080) and an elastomeric polyurethane resin (such as the Estane X-1 or X-2) but then add a melamine-formaldehyde resin (such as Reichold Chemicals' Super-Beckamine, or one made in-house by reacting urea, formaldehyde, and butanol). After coating and evaporation of solvents, the coated tape is put in an oven at 80degC for 24 hours. The polyurethane itself is pre-polymerized, but high temperature results in setting of the melamine-formaldehyde resin.

It is not known if this was ever used in any commercial tapes; the high setting temperature is likely to have been an issue for large scale production. However, in reference [33] the thermosetting mixture from this patent is used as one of the examples of typical formulations which implies it was used extensively.

3.8 Urethane/Vinylidene Chloride/Acrylonitrile Phenoxy Copolymer

A still more sophisticated copolymer was patented in 1975, again by Ampex[21], this time adding phenoxy resin to the mixture creating a four-part polymer. Their example employs Estane 5701 or Estane 5704 (a replacement for the earlier Estane resins), Union Carbide's PKHH phenoxy resin, and Saran F-120 and a polyisocyanate is added (the patent suggests Mobay's Mondur CB-75) in order to promote crosslinking. This solution is suggested to produce a flatter and more glossy surface than previous binders, as needed for cassettes and videotapes.

Some discussion of the effects of the addition of PKHH can be found in [16].

Engineers at TDK in Japan described a variant of this chemistry in a later 1981 patent. They show a three-part resin made of "Nippolan 5033" polyurethane resin from Nippon Polyurethane Ind., "PKHC" phenoxy resin made by UCC, and a vinyl chloride-vinylidene chloride resin "1000WK" made by Denki Kagaku Kogyo, along with a lubricant and solvents[26]. This is not substantially different than the earlier Ampex patent but this patent contains useful information about predicting characteristics from the ratios of the three resins[26]. Other details in this patent imply that it was intended for use in cassette formulations.

3.9 Ampex 406 Binder: Thermosetting Urethane

In 1970, Ampex introduced 406, the first of a set of new audio mastering tapes which had two major new features: urethane binders and backcoating.

The binder for this tape appears to be the one described in the Diaz patent[17]. This formulation is a urethane using Goodyear Vitel PE-207 polyester resin and Spencer Kellogg DV-1088 isocyanate prepolymer which react upon mixing. There are no other crosslinking agents or copolymers. After coating, the tape is heated to finally cure the thermosetting polymer.

The patent describes this binder as initially being designed for use with video tapes in order to obtain improved durability, but it appears to have been used later for audio tapes in order to obtain increased pigment load.

This binder appears to be the first of the widely-used thermosetting polymers, if the patent is to be believed.

The thermosetting binder was promoted because it was more flexible and more cohesive. More oxide could be put into the slurry and the coating could be made much thicker, allowing higher operating levels.

The backcoating provided a rough surface on the back of the tape which allowed a more even tape pack on fast winding. It was expected to have little effect at lower tape speeds. Within a few years, other tape manufacturers had adopted Ampex's technology.

In the 1980s it was found that many products made from urethanes were breaking down and becoming gummy. Speaker surrounds made of urethane foam were turning to goo. Pinch rollers on tape machines and bushings on auto suspensions were becoming soft and cracking as urethanes without sufficient crosslinking were depolymerizing under environmental conditions.

Manufacturers became aware of these problems and many changed formulations to improve stability although not before millions of reels of unstable tape had been released on an unsuspecting public.

3.10 Double Urethane Binder

In 1973, DuPont patented a tape binder which employed a complete preformed nonreactive thermoplastic urethane, mixed with a polyol and an isocyanate which themselves react to form a thermosetting urethane compound. This is claimed to give better wear resistance[28].

The sample formulas given in the patent do not specifically mention industrial products but should be sufficient to replicate the basic process.

It is unknown to this author whether this process was used at any time for audio tapes. It would be difficult to determine chemically or physically since both elements are chemically quite similar.

3.11 Polyester-Urethane/Vinyl Chloride/Vinyl Acetate/Vinyl Alcohol

By 1993 newer polyester-urethane resins had become commercially available, such as B.F. Goodrich's 5701Fl. Ampex chemists, who at the time were very concerned with managing sticky shed, came up with a four-part formulation in an attempt to raise glass transition temperature of the slurry in the belief this would improve stability[24].

They proposed a composition of the aforementioned 5701Fl polyester resin, along with VAGH, a Union Carbide terpolymer of vinyl chloride, vinyl acetate, and vinyl alcohol, and the Mobay CB-701 isocyanate. The resulting copolymer is very hard and stable. A discussion of the effects of VAGH in urethane polymers can be seen in [16].

Another variant they describe add an additional vinyl polymer, the Union Carbide VP-200.

It is unknown whether this formulation was actually used in any production audio tapes as it came at a time when production was beginning to fall off dramatically; the Ampex Magnetic Media division, later Quantegy, had only twelve years to live when this patent was issued and it spent most of those years struggling to make existing products. They were only to release one new audio tape after this patent was issued, that being GP9 which was introduced in fall of 1998. So if this formulation was ever actually used, it would have been in GP9.

3.12 Other Urethane Copolymers

3.13 Rubber-Phenolic Binders

In a 1962 IBM patent[25], manufacture of tape binders employing butadiene-acrylonitrile copolymers and phenol-resorcinol-formaldehyde resins are described as being an existing technology. It is suggested that these are appropriate for high speed computer tapes because of their resistance to wear, but that pressure flow of the binder will cause stiction if the head is kept in a single position on the tape for long.

The patent authors then go on to describe the use of an isocyanate to improve curing of the binder. They describe what appears to be an early thermosetting system. The formula in the patent involves a 3-1 butadiene-acrylonitrile copolymer, an undescribed phenolic resin, lecithin as a dispersant, polymethylsiloxane as a lubricant, methylene-bis-disphenyl-diisocyanate as an accelerant, and acetyl chloride to slow down the reaction.

This binder may have been used for some computer tapes but if so was shortly replaced by more modern urethanes. Such a binder has not been seen by this author in any audio tapes.

3.14 Water-Soluble Binders

In the 1990s some amount of research was performed on tapes with water-base binders, with the intention of eliminating solvents from the manufacturing process. It is not clear if any tapes were ever made with these binders, but certainly it has not been used for any audio tapes.

An latex binder can be seen in [40], an acrylic one in [41], while a polyurethane/vinyl chloride copolymer binder can be seen in [42]. Basic formulations can be found in these papers but will not be repeated here due to general lack of utility. It is surmised that setting time on all of these will be very slow even with elevated temperature curing.

4 Backcoating

Backcoating was introduced by Ampex at about the same time as the urethane binders. Again, first it appeared on videotapes, then later on audio and instrumentation tapes. Backcoating is a rough surface coating on the rear of the tape which causes air turbulence

when air is forced across the tape. This results in more even tape pack when the tape is fast-wound.

It has been stated [7,8] that the backcoating uses the same binder chemistry and that the tape emulsion is the same front and back with the exception of the magnetic pigment on the backcoating being replaced with carbon black and/or silicic acid. This may not be the case on all tapes but seems to have been a common industry practice. Likely more solvent was used in the backcoating slurry to make a thinner mixture since the thickness of the backcoating was far less than that of the front coating.

One author [9] has stated that mechanical removal of backcoating eliminates sticky-shed syndrome. If this is the case, it would indicate that either carbon black or silicic acid are implicated in the breakdown of the binder or that iron oxide is somehow acting to stabilize the binder. This would be a good field for additional research.

It has been shown that test tape formulations made with CrO₂ in place of ferric oxide show reduced stability, but this appears to be the result of CrO₂ acting as an oxidizing agent to degrade the binder, rather than the ferric oxide acting as a stabilizing agent[38].

5 Pigments

The coatings chemists who initially created the first postwar magnetic tapes at 3M were paint people, and consequently we still use leftover terminology from the paint industry. To this day, we call the load of magnetic material in the binder the "pigment."

The pigment makes up a large portion of the tape coating, and correspondingly affects the mixing and coating characteristics of the slurry. This may mean additional components need to be added to the slurry to affect dispersion or that the total percentage of pigment may be limited by the binder [10].

I list only very short discussions of the various popular pigments as their chemistry is mostly not interesting even though they are critical to tape functioning. Far more detail can be found in Mee and Daniels [11].

5.1 Carbonyl Iron

Carbonyl iron is a finely divided powder of elemental iron created by decomposition of purified $Fe(CO)_5$. It was first created in 1925 by BASF and is almost pure iron with minimal carbon and oxygen. It was initially used in some early magnetic tapes but poor magnetic characteristics caused it to be almost immediately replaced with ferric oxides.

These tapes, however, could be considered the distant precursor of modern metal particle tapes.

5.2 Red Oxide

There are multiple oxides of iron, which contributes to the wide variety of color tones in rusted steel. Only one of them has been widely used for magnetic media.

In the production of the first postwar tapes, gamma ferric oxide, $\gamma-Fe_2O_3$ was picked by 3M as having a good B-H curve and being readily available as a paint pigment. The classic "red barn paint" used FeO_3 pigment. Although particle size and distribution changed, red oxide $\gamma-Fe_2O_3$ pigments continued to be used for some magnetic tapes until the end of production.

Early tapes used cubical particles but it was very quickly found that elongated needle-like particles, aligned during coating, gave much better high frequency performance and that such particles could be formed by simple ball-milling of the oxide. An early discussion of the importance of particle shape and configuration can be seen in [35].

Red oxide tapes can be distinguished by the the low operating level and measured coercivity.

5.3 "Black" Oxide

Black iron oxide, Fe_3O_4 was used in early Magnetophon tape, and was adopted by 3M in their #100 paper tape but was quickly abandoned in favor of red oxide.

In the 1960s, Low Noise High Output tape became available with a higher coercivity than conventional $\gamma-Fe_2O_3$. These tapes had a dark or black coating on them and common wisdom held that they were made with Fe_3O_4 .

This appears not to have been the case. These second-generation tapes appear to be dark only due to addition

of carbon black. The color is not related to the higher output levels, that is a function of higher pigment load, better dispersion and better orientation.

That is, there was no revolutionary change from "red oxide tapes" to "low noise high output" tapes, it is strictly an evolutionary change, and color cannot be used to determine anything useful about pigment chemistry or predict coercivity.

Fe_3O_4 has poor stability and has not been used in commercial tape coatings since the very early days of magnetic tape. The author would be very interested in any information which may contradict this.

On the other hand, the Audio Cylopedia says that two types of magnetic film exist, the 'reddish-brown standard oxide' and the 'dark green high-output oxide' [32] although with no details about the differences between these. FeO is a dark green color but again is not of any use for audio recording.

5.4 Cobalt-doped oxide

Strictly speaking these should be referred to as "cobalt-modified iron oxides," being gamma ferric oxide particles whose surface has had cobalt ions implanted in it without them being distributed throughout the particle[12]. This gives a corresponding increase in coercivity.

5.5 Chromium Dioxide

The crystalline structure of chromium dioxide made for improved low speed performance and this formulation became popular with cassettes. CrO_2 crystals are long and needlelike and can be oriented perpendicular to the direction of tape motion, giving a very high coercivity and since the head is oriented toward the cross section of the crystal, very good high frequency response at low speeds.

5.6 Metal Particle Tapes

Metal particle tapes consist of fine particles of elemental iron which have been processed in such a way to render them inert and unable to react with the binder or with atmospheric moisture. In most cases this is the result of an oxide layer deliberately formed on each particle in a controlled fashion.

As far as we can determine the first practical metal particle tape was described by Morita of Sony in 1966[16], if we discount the prewar use of carbonyl iron for tapes.

Metal particle tapes were used for high output cassettes as well as for various digital and videotape formats.

6 Lubricants and Dispersants

Most tapes, contrary to popular received wisdom, were made without any lubricants. At times graphite and silicone polymers have been used on tapes in applications where wear was important such as in broadcast cartridges. Myristic acid and butoxy ethyl stearate have also been used[24].

Also mentioned in the open literature are squalane, squalene, petrolatum, stearyl butyrate, butoxyethyl stearate, n-butyl laurate, methoxyethyl oleate, n-butyl ricinoleate, tetrahydrofurfuryl oleate, stearyl ester of dimethylpolysiloxane, bis(2-ethylhexyl)isobutylacetyl, and sperm oil[33].

A number of rumors of sticky shed having been caused by the removal of “whale oil” have appeared over the years. Although sperm oil (to be distinguished from conventional whale oil or train oil) is mentioned by Kreiselmaier[33] to have been used as a lubricant there is no sign it was ever used extensively in the industry. It possesses a very distinct odor, however, and should be quite detectable. It would not be difficult to do a widespread search for triglycerides on older tapes in an attempt to detect use of animal oils and this would be an interesting ground for research.

Dispersants such as lecithin were frequently used in order to keep an even and constant slurry mix for even deposition on the tape surface. GAFAC RE 610 has also been mentioned as a dispersant used[24]. Other ones referred to in the literature include zinc naphthenate, dioctyl sodium sulfosuccinate, oleic acid, triethenolamine, and lignin sulfonic acid[33].

Note that the lecithin used should be pure lecithin and not an oil-based lecithin solution as contamination from vegetable oils can be a problem with food-grade lecithin. These oils polymerize and work their way to the tape surface causing stiction [16.5].

Adipic acid has also been added to slurries in an attempt to deactivate metal particles left over from processing (most notably ball milling)[24].

The need for dispersants was greatly reduced with the move to urethane coatings. Earlier PVC/PVA coatings had poor adhesion to the pigment unless a dispersant was added.

A good discussion of the physical chemistry involved with the more common lubricant and dispersant agents

can be found in reference [16] and more specific information on dispersants can be found in reference [16.5].

As mentioned before here, carbon black was frequently added either to the backcoating or in smaller amounts to the front coating, to improve conductivity and reduce static pickup. The carbon black provides very little lubrication. A good introduction to the physical chemistry of carbon black in magnetic tapes can be found in [16.5].

Alden[16.7] talks about how Larry Lueck added dry silicone particles to tape formulations in the Scotch 111 era to reduce head clogging from shedding. It would make sense for the binders at the time, but as binders got more advanced and shedding was reduced, it would also make sense for the need for such lubrication to be reduced.

7 Solvents

Needless to say a solvent was required to keep the binder and pigment in suspension for coating. The percentage of solvent in the slurry depended on the viscosity desired which depended on the coating thickness desired and the machinery being used. Mee and Daniels mentions the following as popular solvents: methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, tetrahydrofuran, doxane, n-methyl pyrrolidone, n-dimethyl formamide, and the ubiquitous toluene[13]. Of course, being solvents, these were evaporated and little to no traces of them should be found in the final tape coating. This is mentioned here only for the sake of completeness.

It should be noted that, when new, different tapes have very individual smells and it was not unusual for tape machine operators to identify new tapes out of the box by odor. These smells may also provide some useful clues to tape formulations although to a great extent the smells of new tapes may be a function of the solvents used.

8 Tapes Without Binders

Here we present two interesting special cases of tapes that do not have any conventional binder and rely on somewhat different chemistry.

8.1 Evaporated Metal Tapes

These tapes have no binder but have iron sputtered directly on the base. They were used for some 8mm videotapes as well as for some digital formats.

[I don't know how these were stabilized... surely someone does.]

9 Combined Binder-Pigment

Type L tape, made in Germany for the Magnetophon during the war, is described as an "impregnated material" in that the oxide pigment is embedded into the binder before extrusion of the binder. The performance of this arrangement is very poor due to low oxide loads and the fact that much of the oxide is distanced from the head[31].

10 Conclusion

I have made every attempt here to collect available data from the open literature to explain audio tape formulations over the years. The more common professional recording tapes have been fairly clearly described, while less common tapes and non-audio tapes still are greatly lacking in information. Any information that readers may have to add which can be independently verified would be of great interest.

11 Appendix A: A Basic Tape Timeline

1. Prewar manufacturers made various proprietary formulations
2. BASF made three tapes for the Magnetophon
3. Jack Renner brought a Magnetophon back from Germany and went to 3M to supply tape for it. 3M ignored the existing German tape and used their adhesive tape experience to make an acetate-based tape with a red oxide coating.
- 3.5. A large industry grew up in the US of companies manufacturing tapes based on the basic 3M model of red oxide/PVA/acetate base.
- 3.6. In 1952, Reeves Soundcraft introduced a mylar based tape, and soon other manufacturers followed suit.
4. LNHO coatings became available in the sixties. As mentioned above there were no chemical changes from

previous coatings to this new generation, but there were dramatic physical ones.

5. Video and computer applications required more rugged tapes and several manufacturers did work on urethane and urethane copolymer binders in an attempt to get video and computer tapes that did not shed under the heavy wear of high-speed head travel.

6. Ampex took the research on urethane tapes and realized that a urethane binder would allow them to make an audio tape with a higher ratio of pigment to binder and a thicker coating for higher output. They introduced 406 in 1970.

7. Other manufacturers followed suit and introduced premium mastering tapes using Ampex's chemistry.

8. In the late 1980s sticky shed issues due to improper crosslinking of the urethane binders became common. For a long time neither the nature of the problem nor proper workarounds for tape playback were known, but now both of these are fairly well-established. A discussion of the mechanism can be seen in [50].

9. At the same time, other issues regarding PVA/PVC-binder tapes and some problems regarding non-backcoated urethane tapes became known. These all were lumped together as "loss of lubricant." Most of these failures do not involve lubricants at all but binder failures, and there are a large number of unrelated problems all grouped under this same umbrella. LoL is a misnomer but it's the word people use.

12 Appendix B: Some Recipes

This recipe for magnetic coating comes from Dedell's 1953 SMPTE paper from Kodak[37] and is likely typical of early nitrocellulose-based coatings used on both films and tape:

Nitrocellulose Coating for Magnetic Film	
Ingredient	% wt.
Red Iron Oxide (C.K. Williams IRN-110)	14.0
40-60 SS type Cellulose Nitrate (Hercules Powder Co.)	2.8
Butyl Alcohol	1.2
Cellosolve	8.4
Amyl Acetate (commercial grade)	63.5
Butyl Cellosolve	9.5
Baker's grade AA Castor Oil	0.6

The cellulose nitrate is delivered wet with butyl alcohol (the amount indicated in the formula above). A stock

solution is prepared using this mixture along with the the cellosolve and amyl acetate. The other ingredients are added before use and the mixture ball-milled until a satisfactory dispersion is obtained, likely around 24 hrs. The author notes that very long milling times give poor audio quality but milling up to 150 hrs shows no significant change.

The following three basic recipes for tapes come from Krieselmeier's article in the Pigment Handbook[33]. It would be reasonable to expect these to be typical of tape production in 1973 when it was published:

Thermoplastic Computer Tape Formulation	
Ingredient	% wt.
Magnetic Pigment (Pfizer MO-4328 or HR-280)	34.6
Conductive Carbon Black (Cabot XC-72R or Columbian Carbon Conductex-SC)	2.0
Polyurethane Elastomer Resin (Goodrich Estane 5701)	6.1
Vinylidene Chloride-acrylonitrile copolymer resin (Dow Saran F-120)	6.1
Soya Lecithin	1.8
Silicone Oil	0.3
Tetrahydrofuran	34.4
Toluene	14.7

Prepare slurry of pigments, surfactant and toluene plus enough additional THF to make the slurry (80 K.U.). Disperse in pebble mill for suitable time period such as 15 to 72 hr. Dissolve resins in balance of THF. Add to mill and continue dispersion for 6 to 36 hours. Apply to plastic backing material.

Note the urethane elastomer is pre-polymerized; no extensive chemical reaction is taking place in this process. It is entirely a matter of physical dissolution and then evaporation, though some additional crosslinking may take place. This appears to be an updated version of the formula from the patent in reference [20].

Thermoplastic Audio Tape Formulation	
Ingredient	% wt.
Magnetic Pigment (Pfizer MO-4328 or HR-280)	2.2
Conductive Carbon Black (Cabot XC-72R or Columbian Carbon Conductex-SC)	
Polyester Resin (Goodyear Vitel PE-207)	5.9
Hydrolyzed vinyl chloride/vinyl acetate copolymer resin (Union Carbide VAGH)	2.9
Soya Lecithin	1.8
Methyl Ethyl Ketone	17
Methyl Isobutyl Ketone	34

Prepare slurry of pigments, surfactant and enough additional MIK to make a thin slurry. Disperse in mill for 15 to 72 hr. Dissolve resins in balance of solvent. Add solution to mill. Continue dispersion for additional period of 6 to 36 hours. Remove from mill and apply to plastic backing material.

Note that the oxide material is the same but the oxide load is somewhat greater than with the computer tape above.

Thermosetting Tape Formulation	
Ingredient	% wt.
Mill Charge:	
Magnetic Pigment (Pfizer MO-4328 or HR-280)	36.6
Conductive Carbon Black	2.3
Additives (surfactant, fungicide, lubricant)	2.3
Methyl Ethyl Ketone	5.5
Methyl Isobutyl Ketone	8.7
Let-Down:	
Phenoxy Resin (Union Carbide PKHH)	4.6
Polyurethane Elastomer Resin (Goodrich Estane 5702 or Goodyear TPU-123)	1.6
Urea-Formaldehyde solution (Reichold Chemical Beckamine P196-60, 60% solids)	1.4
Methyl Ethyl Ketone	12.7
Methyl Isobutyl Ketone	2.1
n-butyl alcohol	4.2

Add mill charge to ball mill. Disperse for suitable time period such as 15 to 72 hr. Add let-down solution to mill. Continue dispersion for 6 to 36 hr. Apply to plastic backing. Cure coated tape in oven at 80degC for 24 hr.

Interestingly this also employs an already-polymerized polyurethane resin. It is reminiscent of the formula described in reference [22]. The thermosetting process is that of the linking of the urea-formaldehyde polymer and the linking of that to the existing urethane polymer.

In addition to these three presumably-typical formulae, a vast number of worked-out formulations are listed in the various patents referenced here.

13 Conclusion

There is a lot of existing literature in place regarding chemistry of recording tape materials, and although there seems to be a general feeling among archivists that everything regarding tape manufacturer is proprietary and unavailable, much information is available in the literature. The author has made an attempt to enumerate and summarize much of what is available in open publications.

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