

Pigmentation of Magnetic Tapes

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SCOPE OF APPLICATION

Magnetic tapes consist basically of a very uniform magnetic coating of 0.2 to 0.5 mil thickness bonded to a plastic base. The tape is manufactured in widths from 12 to 48 in. and then slit into ribbons of widths ranging from 0.150 to 2.00 in. depending on the end use.

The market is generally divided into four application areas; audio, computer, video, and instrumentation. The audio segment may be further subdivided into three areas; open reel, endless loop cartridges, and cassettes.

The current worldwide magnetic tape market which exceeded \$400 million in 1972 is expected to grow 10 to 12% yearly and reach a dollar volume of over \$500 million by 1974.¹ The highest growth rate (about 60% per year over the next few years) should be in the cassette tape market. The second highest growth rate of 40% is expected to be achieved by the helical scan videotape market.²

HISTORICAL SURVEY

The first equipment to record information on magnetic media is credited to the Danish

“Edison,” Valdemar Poulsen, in 1893. It used steel wire and an electromagnet. Developments in magnetic recording lagged during the next three decades while essential electronic technology was being developed to amplify very weak signals and make magnetic recording commercially feasible. In 1931 I. G. Farben Co. of Germany commercialized the earlier experiments of Dr. Karl Pfeumer on the coating of powdered materials on both paper and plastic base films by successfully developing a coated tape. The Magnetophone, forerunner of all present day recorders, was first produced in 1935 by Farben. It used plastic based tape running at 30 in./sec. Development of tape technology continued, particularly in Germany during World War II (1939–1945) and extensive use of voice recordings was made by Hitler for propaganda broadcast.

In 1947 the first commercial tape recorders appeared on the market in the United States, and 3M brought out their #100 paper tape with a black oxide tailored to the Magnetophone type machines. In the same year the now widely used red iron oxide was developed. Since that time the growth of magnetic recording and its many applications to its present stature of a \$300 million industry has been amazing. New applications, particularly in the entertainment and educational fields, could provide major impetus for dynamic future growth.

TECHNICAL ASPECTS OF APPLICATION

All magnetic tape from the newest 0.15 in. wide and less than 1 mil thick audio cassette tape; through the familiar $\frac{1}{4}$ in. wide open reel audiotape, to the 2 in. wide video and instrumentation tapes are composed basically of three principal parts: (1) the base or support upon which the magnetic oxides are coated, (2) the magnetic particles which retain the information, and (3) the binder system which provides the cohesive strength between the particles and adhesion to the base.

BASE OR SUPPORT MATERIALS

Since the magnetic coating is generally quite thin (0.2 to 0.5 mil) and has low cohesive tensile strength (100 to 2000 psi), many of the desired qualities of the finished tape are dependent on the quality of the base material. Base films must have a mirror surface finish, free from scratches, ripples, pits, or bumps. They must also be able to stand the high stresses imposed by the recorders and should be of such nature that the oxide coating will strongly adhere to the base and will not flake off. Adhesive intermediate or subbing layers of vinylidene chloride-acrylonitrile³ or butadiene-acrylonitrile⁴ have been used to improve this adhesion.

In addition the base should not readily tear or stretch under normal stresses. It should not support fungus growth, should be nonflammable, should be capable of being manufactured to close tolerances, and should be very flexible both before and after coating. The base should also be unaffected by changes in humidity and should be stable in storage. Enough conductivity should be present so that electrostatic charges do not build up and attract dust particles. Unfortunately, no base film meets all these ideal specifications.

The first base material used, supercalendared brown kraft paper, did not stretch or become brittle, but it did tear easily when

nicked and was also noisy due to surface unevenness.

Cellulose acetate became the most widely used base material for many years. Its dimensions can be held to within 0.0003 in. during manufacture and it is available with a mirror surface. Its yield point and stretch point are very close so that no information is lost due to a stretched tape. The tape simply breaks and can then be repaired with splicing tape. Plasticizers and stabilizers must be compounded with the acetate to give the required flexibility and stability.

Polyester or more specifically polyethylene terephthalate film (Mylar, Celanar, Melinex, etc.) has overtaken acetate film in recent years and continues to grow in usage each year. Since no plasticizers are needed for pliability, the film has high stability and strength. These properties are maintained through many humidity and temperature cycles so less care is required in storage.

By an unbalanced stretching of a substantially amorphous polymeric linear terephthalate ester film, very large increases in the tensile strength, tensile modulus, and most importantly in the tear strength can be achieved. The actual process consists of stretching the cast film 400% in one direction at a temperature of 80 to 100°C and then stretching it about 160% in the transverse direction at the same temperature. The film is then heat set at a temperature between 150 and 200°C while under sufficient tension to maintain the new dimensions.⁵ The resulting film is clear, transparent, flexible, and has a uniform gauge or thickness across its width. It is thus well suited to serve as a base for video, instrumentation, computer, and long play, thin audio tapes.

Polyvinyl chloride has been widely used as a base in Germany, but has not gained acceptance in the United States. It has excellent wind characteristics but is prone to stretch, although it will recover after a period of time. The German Luvitherm is a biaxially tensilized form of polyvinyl chloride.

THE BINDER SYSTEM

The function of the binder is to provide cohesive strength between magnetic oxide particles and strong adhesion between the coating and the base material. The formulation of a good binder system is a combination of art and science because of the many conflicting properties desired in the finished coating. If not done properly the coating may flake off when bent; the tape surface may become tacky and adhere layer-to-layer; or abrasion products may collect on the head and redeposit in the form of lumps on the coating surface, which lift the tape away from the magnetic gaps on the head.

Much formulation and processing technology has been borrowed from the paint industry, but the unique requirements that must be met by the magnetic coating have carried tape formulation and processing well beyond conventional paint technology.

Resins

The resins used in the binder system may consist of one or a combination of polymers such as vinyl acetate, ethyl cellulose, polyvinyl chloride, polyacrylate, polyesters, polycarbonates, polyurethanes, polyamides, phenoxies, or epoxies. In addition, copolymers such as vinyl chloride/vinyl acetate, ethyl methacrylate/ethyl acrylate, styrene/acrylonitrile, vinylidene chloride/acrylonitrile, butadiene/acrylonitrile, and butadiene/styrene have all been used at times as binder resins. Useful binders are often combinations of semirigid or "crystalline" polymers modified with various elastomeric resins.

If applications requiring resistance to friction heat such as stop-action video are encountered, then, thermosetting resin systems such as epoxy-biphenol or urea-formaldehyde cured with polyamide resins or triethylene tetramine are used to yield flexible, thermally-stable coatings.⁶

In cases where high abrasion-resistance is needed, blocked isocyanate prepolymers may be reacted with resins containing hydroxyl groups to produce polyurethane

polymers.⁷ Generally the curing or cross-linking is done after coating and orientation since the attendant viscosity increase hinders leveling and alignment of the magnetic particles.

Wetting Agent

A wetting or dispersing agent is generally added to assist in wetting out (displacing of absorbed gases) and dispersing the pigment agglomerates. The proper choice and application of wetting agent may materially shorten the milling time. The usual concentration range is 0.5 to 10% of the weight of oxide in the batch. Various dispersants and combinations of dispersants have been used with their various advantages and disadvantages. Some of those which have been suggested for iron oxide are: zinc naphthenate; dioctyl sodium sulfosuccinate; the mono-, di-, and triesters of oleic acid and triethanol amine; lignin sulfonic acid; and lecithin. It has been recommended in a patent⁸ that lecithin should be reacted with drying oils such as tung oil, oiticica oil, or dehydrated castor oil to prevent migration to the surface of the coating with a resulting stickiness and tackiness that increases starting time and wear rate.

Lubricant

Lubricants are added to reduce headwear and extend tape life. They also may reduce any tendency for layer-to-layer adhesion which the binder may exhibit. Silicones have been highly publicized; however, other less expensive lubricants are often used in particular applications with much success. Such lubricants as squalane ($C_{30}H_{62}$), squalene ($C_{30}H_{50}$), petrolatum (a C_{20-22} hydrocarbon),⁹ stearyl butyrate, butoxyethyl stearate, *n*-butyl laurate, methoxyethyl oleate, *n*-butyl ricinoleate, tetrahydrofurfuryl oleate, stearyl ester of dimethyl polysiloxane,¹⁰ bis(2-ethylhexyl)isobutylacetal,¹¹ sperm oil, and some solids such as Teflon or graphite have all been recommended.

Stabilizers

Some resins such as the vinyl chlorides are not thermally or age stable, particularly in the presence of iron compounds. Commercial stabilizers for these polymers are used to slow the autocatalytic decomposition reactions involved. Where the application involves an elevated temperature or processing in iron or steel equipment, it is preferable to eliminate this type of resin from the formulation.

Plasticizers

In cases where hard vinyl resins or cellulose esters or ethers are used, it may be necessary to add conventional plasticizers, such as phthalates, which are normally recommended for these particular resins. However, a more desirable approach which avoids migration problems is to add an elastomeric resin such as "nitrile rubber" to internally plasticize the binder.

Solvents and Diluents

The solvent system must meet several criteria. It must hold all solubles in solution and it must maintain pigment dispersion. Diluents should have higher evaporation rates than the true solvents to avoid premature resin precipitation or fractionation. The solvent system should dry fast enough to allow reasonable oven lengths and web speeds. However, too fast an evaporation rate can cause problems in the coating and drying operations.

The most commonly used solvents are methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone. Some of the newer, tougher resins such as thermoplastic polyurethanes require more active solvents such as dioxane, tetrahydrofuran, or *N*-dimethylformamide. These solvents have such disadvantages as cost, toxicity, and tendency to peroxide formation.

Toluene is probably the most common diluent used.

CONDUCTIVE AGENTS

Although conductivity is generally added by including high-structure, high-purity carbon black pigment, various organic antistatic agents have been suggested. The danger is that they may reduce the adhesion of the coating to the base film.

An organic antistatic agent recommended in the patent literature for magnetic tape is di(1- β -hydroxyethyl-2-undeclimidazole)adipate. It is made by reacting the free base of the imidazole with adipic acid. Sebacic acid may also be used as an alternate reactant.¹²

PIGMENTS

Generally two pigments are included in the coating, a magnetic pigment and a conductive pigment. The most common magnetic pigment employed is red iron oxide or acicular γ -ferric oxide. Recently high purity chromium dioxide has begun to replace γ -Fe₂O₃ in some applications such as extended play tapes where its higher magnetic moment per unit volume and higher coercivity permit the use of thinner base material, thinner coatings, and lower tape speeds. These pigments are discussed in greater detail subsequently.

Other magnetic materials such as cobalt-doped γ -ferric oxide,¹³ acicular iron, cobalt, and nickel particles or alloys have been mentioned^{14,15} but none has yet achieved commercial prominence. However, 3M Company recently introduced a line of cobalt-doped γ -ferric oxide tapes for applications requiring improved high frequency response and better signal-to-noise ratios. A fine particle size, high energy cobalt-base metal alloy, trade named Cobaloy (developed by Cobaloy Corporation, Division of Graham Magnetics, Inc.) should also become commercially available in 1973.

The resistivity requirement, which insures the discharge of static electricity, generally ranges from 5×10^5 to $5 \times 10^8 \Omega$ /

square. A low weight percent of high-structured conductive carbon blacks milled into the formulation usually satisfies this requirement.

CONTRIBUTION OF THE PIGMENT TO THE COATING

The heart of the tape and recording process is the magnetic oxide coating which holds the digital or analog patterns laid down by the recording head. Although the magnetic oxide most used is reddish brown iron oxide, it is not the familiar iron rust. Instead it is a synthetic or man-made oxide produced by a chemical precipitation or reduction reaction which gives tight control of such parameters as particle size and shape, crystalline form, density, surface area, and magnetic properties which are of critical importance in the manufacture of satisfactory magnetic coatings.^{16,17}

The magnetic oxide pigment content ranges from 60 to 80%w or from 40 to 50%v of the dried coating. The lower percentage is used in applications where fine, higher-surface area-particles are needed.

GENERAL CRITERIA FOR PIGMENT SELECTION

Generally magnetic iron oxides range in price from 40¢ to \$1.00/lb with the finer particles costing more due to the increased difficulties encountered in processing the colloidal material. These oxides are available from several producers in this country (PFZ, IMP, CBN) in various particle sizes, shapes, densities, and surface treatment. Generally they are supplied in 50 lb bags or drums.

The key magnetic properties required of the pigment are related to the desired recording and erasing characteristics. Most often the coercivity (H_c) of the particles lies between 250 and 320 oersteds (see glossary at end for discussion of magnetic quantities). Some thin, low noise, and low print-

through tapes use oxides with the H_c approaching 500 oersteds. Cobalt-doped γ -ferric oxides have H_c values between 280 and 1,000 oersteds depending on the cobalt content. Cobaloy is produced with H_c values ranging between 500 and 1150 oersteds. The ratio of B_r (remanent induction) to B_s (induction at saturation) or the squareness ratio should be above 0.7 for the oriented coating. An unoriented coating with the magnetic particles randomly dispersed will have a squareness ratio of 0.5.

In addition to the requirement that the value of B_r should approach that of B_s , B_s should be as high as possible in order to maximize the potential B_r of the oxide. The value of B_r generally ranges from 1000 to 1200 gauss in commercial γ -ferric oxide pigmented tapes. The early German tapes used iron oxides which were γ -hematite, cubic or equant in shape. Work in the 1930s and 1940s showed that acicular (needle)-shaped oxides of submicron particle size gave higher values of coercivity, better stability to oxidation, and higher remanence. In addition they were much easier to orient during manufacture. These acicular anisotropic particles can be produced in either black magnetite (Fe_3O_4) or reddish brown γ -hematite (Fe_2O_3), single domain form. The poor chemical stability of the black magnetite as evidenced by its tendency to oxidize at room temperature has largely eliminated its use from magnetic tape coatings. The usual process for manufacturing γ - Fe_2O_3 actually involves a controlled oxidation step which converts acicular Fe_3O_4 to the γ -ferric oxide.

Recently considerable development work has been done on a new, highly acicular (length to width ratio of 8:1) chromium dioxide that was first discovered by DuPont researchers.¹⁸ It has a coercivity in the range of 360 to 500 oersteds and a remanence up to 1600 gauss. This higher remanence and coercivity permits the use of thinner coatings with the same signal output and better resolution or high frequency response. This oxide is also said to be more easily dispersed and to be available in a

narrower range of particle sizes. This leads to very smooth coatings with squareness ratios as high as 0.90. Added benefits are low noise and low print-through.¹⁹ However, long term stability to oxidation may be a problem with this thermodynamically unstable material and could limit its applications. The high hardness of this oxide compared to γ -ferric oxide has also caused some concern about its abrasiveness in high tape speed applications although proper coating techniques are claimed to minimize this problem. New, extremely hard, hot-pressed ferrite tape heads, that last at least 10 times longer than mu-metal heads, should reduce the concern about the abrasiveness of this new tape material. Chromium oxide is commercially available in the United States only under license from DuPont.

PRESENT PATTERN OF PIGMENT CONSUMPTION

The majority of magnetic pigments used today are composed of γ - Fe_2O_3 particles with an average length of 0.3 to 0.4 μ and a length to width or aspect ratio of 4 to 6. Instrumentation, video, and low-speed audio applications, where low noise and increased frequency response are required, use a smaller 0.2 μ long particle. Cobaloy particles are less than 0.1 μm long and have superior low-noise properties. They are also much softer than oxides and thus are potentially the least abrasive of the magnetic particles. Demand is growing rapidly for these smaller particle sizes.

FORMULATION PARAMETERS

Proportion of Pigment in Product

The proportion of pigment in a tape coating usually ranges between 60 and 80%w of the nonvolatiles. Pigmentation of high-density coatings for computer and high output audio will be at the high end of the range while fine particle oxides with their greater surface areas and binder demand

will be at the lower end of the range. Generally the oxide is dispersed only with the solvent and the dispersing or wetting agent (slush grind) or with up to 20%w of resin to stabilize the dispersion. The optimum concentration of resin may be determined by methods similar to the Daniels Flow Point procedure.²⁰ The balance of the resin is added during the let-down step. Hence the pigment content in the dispersion equipment can remain relatively constant for many applications.

The service life of the tape is greatly affected by the final pigment content. Even 1 or 2% excess over the critical pigment volume concentration can cause a sharp drop in the tensile strength, elongation, and adhesion of the coating. The abrasion-resistance in turn will then be greatly reduced and the tape will show excessive rub-off and a shortened life.

Pigment loadings toward the lower end of the range (60–65%) show greatly increased toughness and resistance to abrasion, but the signal output is lowered as a result of the lower remanent flux density. A compromise around 68 to 70%w is generally made where wear-resistance is important. A loading up to 80%w may be used in audio applications where high signal output and frequency response is of greater importance than long-term life. Some producers have begun offering tapes with the conductive carbon black on the back side of the substrate. This allows an increase in the loading of magnetic material with accompanying greater signal output.

INTERRELATIONSHIP AMONG INGREDIENTS

Many of the binders used in magnetic coatings are not good pigment "wettters" or dispersion stabilizers; thus wetting agents are frequently required. The levels range from 0.5 to 10%w depending on the vehicle system. Resins with polar groups such as carboxyl or amino groups are particularly effective as pigment "wettters" and dispersion vehicles. The use of this type of resin

as one of the vehicle solids can speed up the dispersion phase and actually increase the density of the dried coating. Melamine-formaldehyde polymers have been particularly recommended in one patent.²¹

In the case of dispersion vehicles containing high molecular weight polymers, it is possible to fractionate the polymer solution unintentionally during the dispersion operation by preferentially adsorbing the lower molecular weight, more soluble portion on the surface of the oxide particles. This may cause resin agglomeration or gel formation which will act as a glue between pigment particles. This type of flocculation is known as tertiary flocculation or agglutination²² and is not completely reversible. On drying, these agglutinates will show up as bumps in the coating.

PROCESSING

The first step in the production of magnetic tape is to produce an extremely uniform mixture of the various components of the coating, namely the oxide, resins, additives, and solvents. Much of the processing technology and equipment to perform this task has been borrowed or adapted from the paint industry.

The first stage of the mixing step involves wetting the oxide with solvent or diluent and wetting agent. In some cases the oxide is loaded in a tank or ball (pebble) mill and the solution is given time to soak through the powder and get between the individual particles. This soaking stage may last up to 2 days. Premixing may also be done with Mogul or Baker-Perkins type mixers or high speed disk impeller dispersers, or even (unconventionally) on 3-roll mills before transferring the reasonable homogeneous slurry to a ball or pebble mill. The entire process may also be accomplished in the ball or pebble mill with some increase in processing time. Once the premix is reasonably homogeneous (smooth to the eye) it is ready for the second stage, dispersing.

The function of dispersing is to break up oxide clumps and to distribute the oxide

particles uniformly throughout the resin solution. When completed, the dispersion should pass readily through 1 to 10 μ filters. Any fundamental particle size reduction is to be avoided since the magnetic properties of the coating will be deteriorated. Print-through and noise increases will be particularly apparent.

Dispersion is not an easy operation since the small magnetic particles have a very strong tendency to agglomerate or form into clumps. It is very critical to the successful manufacture of tape that the presence of these clumps in the dried coating be eliminated for they are deleterious to performance in several ways: (1) They will produce noise and a nonuniform signal output. (2) If they protrude from the surface, they will cause signal dropouts. (3) If the resin does not wet and adhere to the particles inside the clump, the clump may create a weak spot in the coating. This is a source of rub-off which collects on heads and guides and may re-deposit back on the tape as a large bump.

In order to obtain a good dispersion, very high shear forces must be generated to overcome the attractive forces and separate the particles so the resin solution may wet the surface of the particles. Ideally the polymers should actually bond to active sites on the surface and effectively encapsulate each individual particle to separate it from its neighbors. This is poorly achieved in practice.

To develop the necessary high shear forces, solid dispersing media are often used which are mechanically agitated. The media may be metallic or ceramic, and may be in the shape of balls, cylinders, rods, or irregular-shaped like sand. Under high agitation these media come close to each other and large shear forces are generated between adjacent surfaces.

The oldest and most common dispersing equipment used in the tape industry is the ball or pebble mill. This and other types of dispersers are usually water-jacketed because most of the energy used in agitation is converted into heat. Viscosity and temperature control can be quite critical in some applications. There are several other

types of dispersers which operate in a similar manner but allow a much higher energy input per volume of slurry and are thus faster. These include the attritor, vibratory ball (cylinder) mill, and sand mill. An added advantage of these latter types of mills is that they yield a more uniform product with a narrower particle size distribution. They are particularly effective in the submicron particle size range. A disadvantage is that resident time is not as easily controlled and a multiple cycle or series operation may be necessary to insure adequate breakdown of all agglomerates. Premix preparation is particularly critical in these short-cycle mills.

The time required to achieve optimum dispersion can vary rather widely, from a few minutes to many days depending on the end application. Audiotape usually requires the shortest time. It is a function of several factors; the degree of agitation or power input per unit volume; the size, shape, and density of media; the percent mill and media load; the amount and type of wetting agent; the type of resin; the type and density of oxide; and the viscosity and other rheological properties of the mix. Operating viscosities are generally in the range of 85 to 110 Krebs units depending on the equipment and media used. Krebs units (KU) measure empirically the viscosity based on the Stormer paddle-type viscometer that is widely used in the paint industry. Additional solvent or resin solution may be needed to adjust the viscosity during the early part of the dispersing stage when pigment surface area is being rapidly exposed and degassed.

The principal production dispersion assessment instrument used by the paint industry, the Hegman gauge, is not satisfactory for evaluating magnetic tape dispersions. The minimum particle size measurable by this gauge is of the order of 2μ where a "good" tape paint dispersion should all pass through a 2μ filter.

Many methods for evaluating pigment dispersions consist of measuring a physical property such as color value, gloss, opacity, or other final properties of the let-down product. A portion of the product may be

applied to a plastic backing, dried, slit, and "played" on a tape recorder. High frequency response and remanent flux density can thus be monitored as a function of the degree of dispersion. All these methods are limited as production controls due to the time required to complete the procedure and obtain the results of the measurements.

In assessing a magnetic dispersion it is preferable to utilize a method based on an examination of the mill base concentrate rather than the diluted final product since the let-down procedure may have a considerable influence on the results. In practice small amounts of mix can be removed at various time intervals and drawn down on a glass slide. The dried coating can then be examined with an optical microscope for the presence of agglomerates. A low-angle glancing light will enhance the contrast and make surface irregularities stand out. The general texture of the coating will also be apparent under this type of lighting.

Cope and Boulton²³ have suggested that a rheological examination of the mill base during processing may be used as a sensitive and rapid method to control particle size and dispersion if testing techniques are rigidly standardized. Their methods seemed to be particularly effective in evaluating mill bases produced by high-energy input dispersers such as high-speed ball mills and Kady mills, which yield pigment particles below 0.5μ in size.

A critical part of the dispersing stage occurs during the let-down or removal from the mill. Efficient operation dictates as high a concentration of pigment in the mill base as practical. Resin content may run from zero to 20% of the pigment weight. The balance of the resin must then be added when the dispersion is judged to be satisfactory. It is generally dissolved in additional solvent and added to the mill base with good agitation.

Opportunities for colloidal shock of the dispersion should be minimized. Good practice calls for adding a let-down medium with a higher solvent strength than the solvent strength of the original grinding medium. In addition the molecular weight of the solvent added should be lower than

of the solvent in the original grinding medium to facilitate the mixing process.²² Generally the let-down paint is milled for an additional period or passed through the continuous disperser for an additional cycle to insure that any pigment flocculates formed are redispersed.

STORAGE

The length of time a mix may be stored is limited by the rate at which the magnetic oxide will either agglomerate or settle out. Polar resins with good pigment absorption properties will significantly slow this rate.

Most thermosetting binders have limited "pot life" because of the cross-linking reaction which often starts even at room temperatures, resulting in either a viscosity increase or gel formation. Incompatibilities between resins may also develop gel particles during storage. If the mix viscosity is low (70–80 KU) and good pigment encapsulation has not been achieved, severe reagglomeration may occur within minutes. However, it is also possible to achieve stable dispersions which have a shelf life of weeks or longer, just as do modern paints. The mix is often agitated or circulated during storage. Refiltering may also be used to remove larger agglomerates or gel particles and "polish" the mix. After extended storage the mix may be redispersed with a relatively short cycle in the proper dispersing mill. Due to the high pigment loading required, the coating fluid will be thixotropic and care must be taken to adjust it to the proper coating viscosity. Constant shear viscometers are preferred over the Stormer paddle unit used widely in the paint industry.

COATING

The function of this step is to apply a very thin, uniform coating of the paint to a web of base film at a speed of 100 to 400 ft/min. The coating should be uniform both along and across the web. Webs as narrow as 12 in. and as wide as 48 in. are commercially

coated. The coating should also be very smooth and free of ridges, bumps, bubbles, pits, and craters. Control of coating thickness is very critical and tolerances may be maintained to less than $\pm 5\%$ based on the dried coating thickness. Depending on the formulation, the wet coating thickness may be 4 to 10 times the dry coating thickness. Resin gel particles or agglutinates contract less than this and can cause a bump in the dried coating. The base film used may be washed or precoated before it reaches the coating head. It may be also run over hot and cold rolls to condition it and eliminate wrinkles and tension lines. The coating equipment actually used can vary greatly with different producers. Reverse roll, knife, and gravure coaters are routinely used.

Immediately after leaving the coating head the coating is passed through a magnetic field for orientation. In audio and computer applications the field lies parallel to the coating direction. Videotapes may be oriented at an angle to the coating direction. The required field strength lies between 500 and 1000 oersteds. Orientation must occur at a processing stage where the viscosity is low enough so that the particles can be rearranged, yet high enough to maintain the alignment after leaving the region of the field.

After orientation the web is passed through a drying oven to remove all solvents and leave the magnetic paint firmly adhered to the base film. Hot filtered air is usually used to sweep the solvents from the coating prior to takeup on a large reel.

Prior to slitting, the tape is generally given a surface treatment to improve the smoothness of the surface of the coating. This operation increases high frequency response and reduces head-to-tape separation (thereby improving output substantially). This may take the form of running the tape between heated, highly polished metal pressure rolls and an elastic paper roll,²⁴ softening it with solvents and pressing the coating against a highly polished roll,²⁵ mechanically grinding and working the surface of the tape against itself,²⁶ or polishing it with high-speed cutters.²⁷

A critical step in the manufacture of precision tape is the slitting operation. The abrasive nature of the fine γ -ferric oxide and the tough character of the polyester-base film make it difficult to achieve a sharp square-cut edge. Almost all slitting of magnetic tape is done by rotary shear cutting. Frequent regrinding of the cutting edge is necessary to maintain accuracy of the cut and prevent rough or nicked edges on the slit ribbons. Careful guidance and tensioning of the ribbons during slitting is necessary to prevent any skewing of the tape as it passes over the heads on a transport.

After slitting, the ribbons are separated and wound onto hubs or reels at constant tension to assure an even wind. Any unevenly wound tapes are rewound on precision tape decks to insure that the finished reel has the correct tension and an attractive appearance.

PERFORMANCE

From reels of finished tape picked at random from each batch, the tape is checked for proper width and thickness of both the coating and the finished tape. The tape is also inspected for cupping or curl and for a biased cut which would cause it to skew on the tape heads. The edges are inspected for smoothness and freedom from cuts or nicks. The coated surface is examined under a microscope to check for conformity to specifications. The coating is also checked for adherence to the base film and absence of flake off. Layer-to-layer adhesion, excess friction, and squealing are evaluated. Tensile strength and tear resistance are also determined. An environmental chamber is used to check whether the reactions of the tape to extremes of temperature and humidity are within acceptable limits.

In addition to these physical tests, the magnetic characteristics must also be checked. The tape must have a uniform output; it must have the proper sensitivity; it must erase properly; its frequency response must be adequate; it must have low noise

levels, proper coercivity, and proper remanence; and finally it must exhibit satisfactory resistance to print-through. The relative importance of these different magnetic characteristics will vary with the end application.

Audio applications require a tape which performs within the operating range of bias and record currents of present recording equipment (some recently manufactured cassette recorders include a switch to adjust the bias currents and equalization circuitry for either conventional γ -iron oxide or chromium oxide coated types). The frequency range should run from 20 Hz to 20 kHz. Low noise and low third harmonic distortion are also required along with a wide dynamic range.

In addition to the general physical tests detailed above, videotape must meet important performance parameters of headwear, tapewear, dropouts, clog, and shed as discussed below.

Video heads have narrow gaps and are quite subject to headwear since they travel at high speeds relative to the tape surface. Up to 3 mils wear may be allowed before head replacement becomes necessary at high cost. Since γ -ferric oxide is abrasive, careful control of processing parameters, particularly during the dispersion stage, is necessary to keep headwear low while maintaining the desirable magnetic properties.

Tapewear is evidenced by excessive dropouts, clog, shed, or deterioration of other properties. It is a function of formulation and processing procedures. A good commercial videotape will withstand thousands of passes across a head in the testing laboratory before the "end of life" point is reached. Repeated handling damage in actual field use can end the useful life of a tape long before the excess wear point is reached.

A poorly formulated tape may actually clog or bridge the gap between pole pieces, causing them to partially or completely short out and become inoperable. These wear products collected on the head may also redeposit on the tape as a bump which displaces the tape from the head and causes a loss of signal.

Shed is evidenced by a powdery deposit on the guides and around the head assembly. If excessive or tacky, it can also redeposit and fuse onto the tape as a bump. Shed results from edge damage, poor slitting, poor coating adhesion, or an excessively weak or brittle coating.

Dropouts are evidenced by white horizontal streaks on the video picture due to momentary loss of signal. Dropouts may be caused by dust contamination, by agglomerates or voids in the tape coating, or by redeposited particles of coating or base film which cause the tape to be momentarily displaced from the head. Skillful formulation and control of the whole manufacturing process are necessary to prevent the occurrence of dropouts in the tape. Generally, commercial videotape recorders are deliberately adapted to rigorously test the tapes to insure they exceed the above performance criteria.

The critical requirement for computer tape is freedom from errors even after extended use. An error may be either a loss or "dropout" of signal or the spurious addition or "dropin" of one or more noise spikes. Present computer tapes are individually tested on a transport and sold certified to be free of errors at packing densities of 800 or 1600 bits/in. for phase modulation.

In addition, computer tape must be able to survive rapid acceleration and deceleration forces. Careful control of static and dynamic friction between the coated and base sides of the tape are necessary to avoid cinching—the slippage of part of the pack on the reel with respect to the adjacent sections. This can result in damage to the tape and thus interfere with the retrieval of recorded information. Recently audio, video, and computer tapes have appeared which have a thin conductive carbon black coating on the back side of the ribbon. The surface of this coating can be textured so that it tends to "lock" into the adjacent magnetic oxide coating and largely prevent slippage of the pack. Added advantages of the coating are that polyester rub-off from the back side of the tape is largely eliminated and the carbon black conductivity prevents any

static charge buildup, which tends to attract dust particles from the air.

Poorly controlled slitting can also be detrimental. In addition to dusting and contamination from rough edges, width error or skew can cause misalignment on the tape head. Furthermore, skew can cause a time-displacement error among the tracks on the tape. Skew is generally determined by dynamic tests on a transport.

The magnetic computer tape coating must also be conductive enough to prevent the buildup of static electricity which will cause clinging on the transport and attract contaminant particles. The resistance is adjusted to 5×10^5 to $5 \times 10^7 \Omega/\text{square}$.

Finally cleanliness, a uniform coating thickness, no shed, no agglomerate nodules, and no gel particles are all obvious requirements for a saleable tape.

The critical requirement on instrumentation tape is surface smoothness. The output of a 60 $\mu\text{in.}$ wavelength signal (equivalent to a 2 Mc frequency at a tape speed of 120 in./sec) will drop some 27dB with a head-to-tape separation of only 30 $\mu\text{in.}$ Peak-to-valley variations of less than 5 $\mu\text{in.}$ are characteristic of quality instrumentation tapes.

In addition, the very narrow gap between pole pieces on a wide band reproduce-head brings added sensitivity to clog and headwear (see video section above). Freedom from skew, low print-through, and extreme cleanliness are also important. An ability to tolerate a wide environmental temperature range from +40 to 125°F is also required.

TYPICAL FORMULATIONS FOR MAGNETIC COATINGS

Typical formulations for magnetic coatings are given in Tables 1, 2, and 3. The number superscripts in these tables refer to the following suppliers:

1. Charles Pfizer
2. Hercules
3. Cabot

Table 1 Thermoplastic Computer Tape Formulation^a

	%w
Solids	
Magnetic pigment (MO-4328 ¹ or HR-280 ²)	34.6
Conductive carbon black (XC-72R ³ or Conductex-SC ⁴)	2.0
Polyurethane elastomer resin (Estane 5701 ⁵)	6.1
Vinylidene chloride-acrylonitrile copolymer resin (Saran F-120 ⁶)	6.1
Soya lecithin	1.8
Silicone oil	0.3
Solvents	
Tetrahydrofuran	34.4
Toluene	14.7
	Total = 100.0

^aPrepare slurry of pigments, surfactant, and toluene plus enough additional THF to make thin 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 hr. Apply to plastic backing material.

4. Columbian Carbon
5. B. F. Goodrich
6. Dow Chemical
7. Goodyear Chemical
8. Union Carbide
9. Reichhold Chemical

The formulations of Tables 1, 2, and 3 are provided for illustrative purposes only. Some are covered, at least in part, by recently issued patents such as U.S. 3,144,352 and U.S. 3,320,090 (both to Ampex).

GLOSSARY OF TERMS

The response of a magnetic tape to a magnetic field is not linear but follows a hysteresis loop as shown in Fig. 1. The terms relating to this cycling process and other technical terms used in the text are defined in this glossary.

Coating Resistance (Ω /square or Ω/\square)

This term refers to the electrical resistance of the coating measured between two paral-

Table 2 Thermoplastic Audiotape Formulation^a

	%w
Solids	
Magnetic oxide (MO-4328 ¹ or HR-280 ²)	37.0
Conductive carbon black (XC-72R ³ or Conductex-SC ⁴)	2.2
Polyester resin (Vitel PE-207 ⁷)	5.9
Hydrolyzed vinyl chloride-vinyl acetate copolymer resin (VAGH ⁸)	2.9
Soya lecithin	1.0
Solvents	
Methyl ethyl ketone	17.0
Methyl isobutyl ketone	34.0
	Total = 100.0

^aPrepare slurry of pigments, surfactant, and enough methyl isobutyl ketone 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 hr. Remove from mill and apply to plastic backing material.

Table 3 Thermoset Tape Formulation^a

	%w
Mill Charge	
Magnetic pigment (MO-4328 ¹ or HR-280 ²)	36.6
Conductive carbon black	2.3
Additives (surfactant, fungicide, lubricant)	2.3
Methyl ethyl ketone	5.5
Methyl isobutyl ketone	8.7
Toluene	11.7
Let-Down	
Phenoxy resin (PKHH ⁸)	4.6
Polyurethane elastomer resin (Estane 5702, ⁵ TPU-123 ⁷)	1.6
Urea-formaldehyde solution (Beckamine P196-60, ⁹ 60% solids)	1.4
Methyl ethyl ketone	12.7
Methyl isobutyl ketone	2.1
Toluene	6.3
<i>n</i> -Butyl alcohol	4.2
	Total = 100.0

^aAdd 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 80°C for 24 hr.

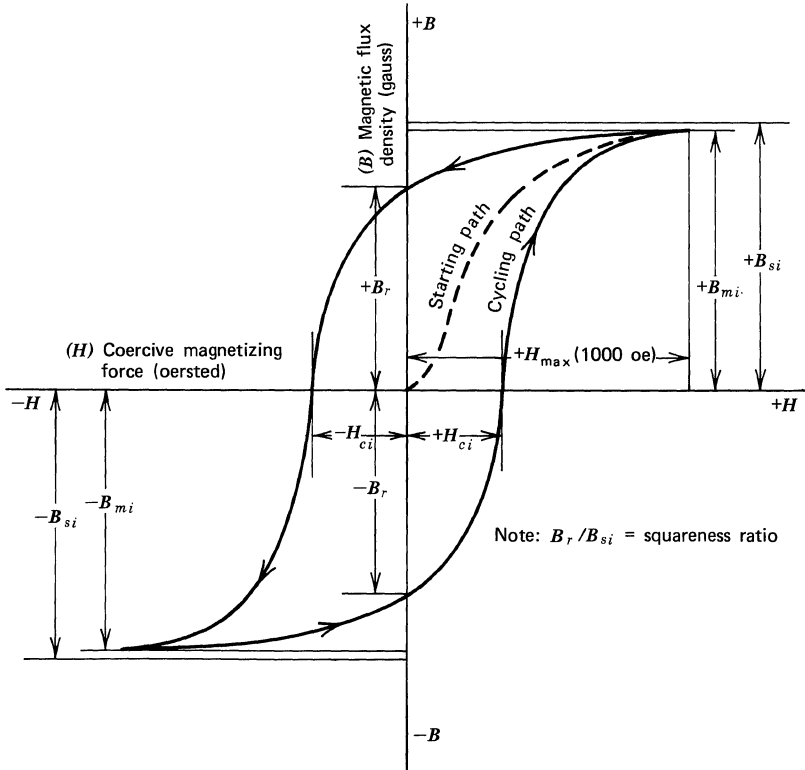


Fig. 1. Representative hysteresis loop showing interrelationship among magnetic quantities.

lel electrodes that are spaced a known distance apart along the length of tape. The resistance of a conductive magnetic coating is usually $100 \text{ M}\Omega/\square$ or less whereas non-conductive coatings have a coating resistance of several thousand $\text{M}\Omega/\square$. Since the resistance is directly proportional to the distance between the electrodes and inversely proportional to the width of the electrodes, the dimensions of the square need not be specified.

Decibels (dB)

A decibel is defined here as a dimensionless unit used for expressing the ratio of two powers, voltages, or currents on a logarithmic scale. One dB represents a difference of about 11.2% between the magnitude of the two quantities. The formula for calculating decibels is given by

$$\text{dB} = 20 \log_{10} (\text{electrical quantity}_1 / \text{electrical quantity}_2) \quad (1)$$

Gauss (G)

A gauss is the cgs unit of magnetic induction equal to 1 maxwell (one line of magnetic force/cm²). Prior to 1932 the term gauss was also used as the emu unit of magnetic field strength, *H*, which is now called as oersted. A gauss meter is a magnetometer that measures the intensity of a magnetic field but not its direction.

Intrinsic Coercive Force (*H_{ci}*)

The magnetizing field strength at the stage where the intrinsic flux density is zero when a sample of magnetic material is in a symmetrically cyclical magnetized condition is referred to as the intrinsic coercive force. Generally the *H_{ci}* of a tape is measured in the orientation direction using a magnetic field strength of 1000 oersteds. The value of *H_{ci}* is the major factor that determines the head currents required to record, bias, or erase a tape.

Intrinsic Flux Density (B_i)

The intrinsic flux density of a magnetic material is the amount by which the normal flux density exceeds the flux density in vacuum for a given value of magnetizing field strength. In the cgs systems of units the intrinsic flux density is equal to the regular flux density less the magnetizing field strength ($B_i = B - H$).

Maximum Intrinsic Flux Density (B_{mi})

The maximum intrinsic flux density is the maximum positive or negative value of the intrinsic flux density when a sample of magnetic material is in a symmetrically, cyclical magnetized state. Generally B_{mi} of a magnetic tape coating is measured in the orientation direction, using an alternating magnetic field of 1000 oe.

Oersted (oe)

An oersted is the cgs unit of magnetic field strength. It was formerly called a gauss (which see for more detail).

Orientation Direction

This refers to the direction in which the acicular magnetic particles are aligned by a uniform magnetic field during the coating process. The orientation direction is longitudinal (parallel to the length) except for systems designed for rotating head use.

Residual Flux Density (B_r), Gauss

B_r is the magnetic flux density when the magnetizing field strength is zero during a cycling process (see hysteresis loop). B_r is generally measured in the orientation direc-

tion using an alternating magnetic field amplitude of 1000 oersted. Residual flux density indicates the output that can be expected from a tape at short wavelengths. Residual flux, the product of B_r times the cross-sectional area, indicates the output that can be expected at long wavelengths.

Saturation Flux Density (B_{si}), Gauss

B_{si} is the maximum intrinsic flux density that is possible in a sample of magnetic material. Since the intrinsic flux density approaches asymptotically the saturation flux density (as the magnetic field strength is increased), a magnetic field strength in excess of 5000 oersted is needed to accurately measure B_{si} in a typical magnetic tape.

Squareness Ratio (B_r/B_{si})

The ratio B_r/B_{si} indicates the extent of particle orientation in tape coatings consisting of oriented, acicular particles. In theory the ratio varies from 0.5 for randomly oriented particles to 1.0 for completely oriented particles. Most oriented tapes have typical ratios between 0.7 and 0.8.

Wavelength (λ)

The wavelength refers to the distance along a recorded tape corresponding to one complete cycle of the sine wave signal. The wavelength recorded is equal to the tape speed divided by the frequency of the recorded signal. If the wavelength is to be given in microinch (10^{-6} in.), then a 2 megacycle (Mc) frequency signal recorded at a tape speed of 120 in./sec has a wavelength of $60 \mu\text{in.} = (120 \text{ in./sec}) (2 \times 10^6 / \text{sec}) = 60 \times 10^{-6}$ in.

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