WHY TAPES STICK: A RATIONALE

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INTRODUCTION:

The purpose of this paper is to describe the application of the chemical reaction theory of adhesion to explain the reduction of stick-contamination of debris from flexible recording media in ¾" tape drives under stressed environmental conditions using an alumina-titania head surface coating.

The condition of stick-contamination of debris from magnetic recording tape has been omnipresent for many years, becoming more severe during the summer months when ambient temperature and relative humidity levels are generally higher. Over the past few years the propensity for stick-contamination with IBM S/500 tape has become greater, requiring more frequent cleaning of the recording head surface and the tape. Recently, some 31/7/7 tape has exhibited a strong tendency to stick. With the advent of higher recording information densities and smaller interblock gaps between data, unsatisfactory error conditions have become more probable. Due to the fact that customers tape libraries represent a constrained "condition" in terms of compatability, attention was focused on modifying the recording head surface characteristics.

For nearly a decade the working surface of ¾" recording heads in tape drives has been electroplated chromium which is subsequently machined, ground and polished to provide a very smooth finish. The double radius contour provides reasonably effective "wiping" action where the Read and Write pole pieces are exposed but also allows for significant amounts of contamination to collect at the approach and exit areas. Certain recording media shed debris which adheres very strongly to the head surface and eventually acquires a "melted" appearance. This debris may also migrate to the tape surfaces and
in some cases result in a "pull-out" of the recording media surface coating.

During the period June - December 1973, a program was implemented to find a head surface coating that the debris would be less likely to stick to.

We found that a plasma-flame sprayed coating containing 60\(^{\text{w/o}}\)Al\(_2\)O\(_3\) and 40\(^{\text{w/o}}\)TiO\(_2\) was manufacturable on heads and provided significant anti-stick improvement over the substituted for electroplated chromium.

MODEL SURFACE DESCRIPTION:

What follows is a brief background for the hypothesis that was developed to explain these results and a progress report on the status of experiments designed to prove or disprove it.

Following Bolger and Michaels work\(^1\), they use a model whose schematic form is shown in Figure I, where the metal oxide surface is both hydroxylated and hydrated. The population of MOH groups is of the order of 1 per 50-100Å\(^2\).

![Model Surface Diagram](image)

**Key:**
- M = Metal Atom
- O = Oxygen
- = -OH
- = H\(_2\)O

**FIG. 1.** Schematic representation of water and oxide layers on metal surface.

Though virtually all metal oxides have a similar surface structure, practically they differ widely in their surface interactions with organic adherates. It is held that this is mostly due to the activity of the surface hydroxyl groups, which in turn is due to the electron density of the oxygen atoms. Whether
the electron density is high or low determines whether the surface reacts as an acid or a base. The identity of the metal atom influences the activity of the OH group through its "electronegativity" (the ability of the oxygen atoms to attract electrons (or donate protons). For a low electron density a variety of reactions may take place; via a dissociative surface reaction:

\[ -\text{MOH} + H_2O \leftrightarrow -\text{MO}^- + H_3O^+ \]

or via a (non-dissociative) adsorption process:

\[ -\text{MOH} + \text{OH}^- \rightarrow \text{MOH} \cdots \text{OH}^- \]

Similarly for a high electron density:

\[ -\text{MOH} + H_2O \rightarrow -\text{MOH}_2 + \text{OH}^- \]
\[ -\text{MOH} + H_3O^+ \rightarrow -\text{MO}^+ \cdots H_3O^+ \]

The equilibria for the above reactions depend both on the solid and on the electrolyte in which it is immersed. The surface charge can be calculated from Zeta potential measurements at various pH levels to determine the zero point of charge or isoelectric point (IEPS) by using suspensions of powered samples in water. IEPS should serve as a qualitative guide to the factors that govern the ability of these surfaces to lose, donate or attract or bind protons in contact with non-aqueous liquids and solids. Parks has found that the IEPS of an oxide can vary over a broad range reflecting:

1. Composition and X-Stalline (or amorphous) form of the oxide
2. Lattice substitutions and impurities
3. Degree of hydration or hydroxylation of the surface
4. State of oxidation or reduction

In general, the valence effect on IEPS may be outlined:

- \( M_2O \) : IEPS > pH 11.5
- \( MO \) : 8.5 < IEPS < 12.5
- \( M_2O_3 \) : 6.5 < IEPS < 10.4
- \( MO_2 \) : 0 < IEPS < 7.5
- \( M_2O_5,MO_3 \) : IEPS < 0.5

Park's plot of IEPS versus \( z/r \), where \( z \) is the cation valence and \( r \) is the cation radius, is shown in Figure II. Hydration increases IEPS; anionic impurities shift in the acid direction, cationic impurities to the basic.
INTERACTIONS WITH ORGANIC MATERIALS:

Bolger and Michaels show that the oxide surface can interact with a polar organic group by a variety of mechanisms. Either the surface hydroxyl or the organic group can act as an acid (proton donor) or as a base (proton acceptor). The bond between the surface group and the organic group can range anywhere from being very weakly ionic to wholly ionic:

\[ A-H \cdots B \rightarrow A^+H^-B \]

An oxide, for example, may interact with a carboxylic group to give either a dipole or an ionic bond:

\[ -MOH + RC-OH \rightarrow \overset{+}{\quad} O \quad \overset{-}{\quad} -MO\cdots HO\cdots CR \]

They have classified the possible interaction into two general interaction types. For type A, the surface provides the basic group which interacts with an organic acid. In type B, the surface provides the acidic group which inter-
acts with an organic base. Within each type they distinguish between two extreme conditions where the interaction is predominantly ionic or non-ionic:

A-1: Dipole interaction with organic acid
\[ -\text{MOH} + \text{HXR} \rightarrow \text{MO}^+\text{H}_2\text{XR} \]

A-2: Ionic interaction with an organic acid
\[ -\text{MOH} + \text{HXR} \rightarrow \text{MO}^+\text{H}_2\text{XR} \]

B-1: Dipole interaction with an organic base
\[ -\text{MOH} + \text{XR} \rightarrow -\text{MOH} \cdot \text{XR} \]

B-2: Ionic interaction with an organic base
\[ -\text{MOH} + \text{XR} \rightarrow -\text{MOH} \cdot \text{XR} \]

X is an electronegative atom usually oxygen or nitrogen. To predict the probability of an interaction for a given oxide surface - polar group combination, they derive a delta, \( \Delta_A \) and \( \Delta_B \), for type A or B interactions which is related to the equilibrium constants for a polar group acid or conjugate base and the IEPS:

\[ \Delta_A = \text{IEPS} - \text{pKa}(A) \]
\[ \Delta_B = \text{pKa}(B) - \text{IEPS} \]

The qualitative relationship between the bond energy and \( \Delta_A \) or \( \Delta_B \) is depicted in Figure III. In Figure IV are shown the dipole orientations, dominant interaction modes and relative bond strengths for a high IEPS surface (MgO) and low IEPS surface (SiO\(_2\)).
CHARACTERIZATION OF TAPE DEBRIS

Over the years considerable analytical work by F. S. deCormier\(^3\) has provided a picture of the functional constitution of debris from S/500 tape. Solvent extraction followed by infrared spectra examination of the extractables shows the presence of varying amounts of unreacted polyester, acrylonitrile and butadiene rubbers, low amounts of polyvinyl chloride, alcohol, acetate and epoxy resins and trace amounts of lubricant plus some substrate particles. The ratio of unreacted polyester to lubricant is generally higher for "stickier" tapes. This tape debris is generally considered to be alcoholic and amine in functionality though minute amounts of carboxyl have been found on the worn tape surface by ESCA. The worn tape surface appears to be lubricant starved at times during use as indicated by an upward shift in surface energy from contact angle data measured by Mittal.

Recently a considerable amount of effort has been placed on the analysis of 3M/777 "sticking" tape.\(^4\) It is evident that "bad" tape contains a large amount of a carboxylic acid functional group and a polyurethane. There is some evidence that the topically applied lubricant is somehow initially "unavailable" at the tape surface since stick occurs most probably on the first pass. In both cases it is held that the deficiency in the tape lubrication is a key reason underlying stick. The approach of modifying the recording heads
running surface is in general thought to be correction of a second order effect. Nevertheless, we find that some improvement can be made by this approach.

PREDICTION OF BEST HEAD SURFACE: S/500 TAPE:

For the purpose of the discussion we consider that S/500 tape debris has an alcohol-amine functional characteristic while 3M/777 tape debris has a dominant carboxylic functionality. Further determination of the molecular weight ranges involved should elucidate the mechanism of the breakdown of the binder system components.

Considering S/500 tape with amine character and an alumina head surface:

\[ \text{IEPS}_{9} \quad pK_{A} = 10, \Delta p = +1 \]

(Ionic interaction with an organic base)

We would experience the above interaction as most probable to form an ionic bond (positive sign). A better choice for the head surface would be nickel oxide (NiO):

\[ \text{IEPS}_{10.5} \quad pK_{B} = 10, \Delta p = -0.5 \]

(Dipole interaction with an organic base)

We would have, then, a dipole (negative sign) type of interaction with a weaker bond as the most probable situation. In the case of alkyl end groups (-OH), all the bonds formed would be of the weak dipole type:

\[ \text{IEPS}_{9} \quad pK_{B} = -4, \Delta p = -13 \]

Thus, for an optimum solution to the S/500 problem of stick we need a basic surface; the more basic the better.

The laboratory test for contamination stick was performed on 729 type drives using a rod holder in place of the head. Correlation with head surfaces on 3420 drive operation was established previously. Acceleration was achieved by a stress environment of 95°F/51% relative humidity. Surface finish of the coated and ground (.200 "dia.) rods was required to be better than 162
20\(\mu\)m peak to valley to avoid "cow-catcher" effects. Similarly, only coatings whose wear rate was less than 100\(\mu\)m/200 full reel passes are considered to avoid "abalative" effects though this point could be arguable on a micro­
basis. Satisfactory qualitative results were obtained on the plasma flame
sprayed coatings following:

\[
\begin{align*}
&A_2O_3 \\
&Cr_2O_3 \\
&3A_2O_3\cdot2SiO_2 \text{(Mullite)} \\
&A_2O_3\cdotMgO \text{ (Spinel-Magnesium Aluminate)} \\
&85w/oA_2O_3-10 w/o MgO-5 w/o TiO_2 \text{(Composite plus blend)} \\
&87w/oA_2O_3-13 w/o TiO_2 \text{(composite powder - Metco #130)} \\
&70w/oA_2O_3-30w/oTiO_2 \text{(Blend - analyzed)} \\
&60w/oA_2O_3-40 w/oTiO_2 \text{(composite powder - Metco #131VF)} \\
&60w/oA_2O_3-35 w/o MgO-5w/oTiO_2 \text{(composite plus blend)}
\end{align*}
\]

As the amount of a more basic oxide (i.e., MgO) was added to \(A_2O_3\) the results were somewhat better compared to those where more acidic oxides (\(TiO_2, SiO_2\)) were added. The 60w/o\(A_2O_3-40w/oTiO_2\) coating met requirements for manufacturability and head life.

The following coatings were found to be unsatisfactory on a qualitative basis:

**Electrodeposited Coatings:**
- Rh, Cr, Sn-Ni(65-35w/o), Ni-P(2-15w/o)

**Sputter Deposited Coatings:**
- SiC, MoS_2, SiO_2, Si_3N_4, GaFe_5O_12

**Ion Plated Coatings:**
- TiC, HfN, Diamond

**Plasma Flame Sprayed Coatings:**
- TiO_2, TiC, ZrB_2
- 50w/o\(A_2O_3\)-50w/oTiO_2 (blend, sieved, analyzed)
- \(Cr_2O_3+\) Trace of Cr metal

It is apparent that metals and alloys, carbides, borides, nitrides, silicides are unsatisfactory. Oxides as acidic as \(TiO_2\) are also unsatisfactory. For
a mixture of Al₂O₃ and TiO₂, the breakpoint is around the 50w/o point, though
the relative wear rates of the two materials may provide a surface composition
richer in alumina than the bulk composition. On balance it is felt that a
neutral to basic surface would be desirable. The test on NiO (IEPS 10.5)
is pending to confirm this and provide more support to the hypothesis.

Prediction of Best Head Surface: 3M/777

Considering 3M/777 tape with a carboxylic character and an alumina surface:

\[ \text{\text{\text{\text{\text{\text{A1O\text{\text{\text{H}}}}}_2\text{O\text{\text{\text{CR}}}}}}}} \]

IEPS=9 \quad \text{pKa}(A)\approx 4.5 \quad \Delta A = +4.5

(Ionic interaction with an organic acid)

We would experience the above interaction as most probable to form an ionic
bond (positive sign). A better choice for the head surface would be a highly
acid surface such as tungsten oxide (W₂O₅) or tantalum pentoxide (Ta₂O₅):

\[ \text{\text{\text{\text{\text{WO\text{\text{\text{H}}}}}_2\text{O\text{\text{\text{CR}}}}}} \]

IEPS=0.5 \quad \text{pKa}(A)\approx 4.5 \quad \Delta A = -4

(Dipole interaction with an organic acid)

The most probable bonds formed would be dipole in nature and thus weaker.
Thus for an optimum solution point of view, an acid surface is needed; the
more acidic the better. It is interesting to note that carboxyl(-COOH) groups
are commonly employed to establish strong chemical bonds to polar surfaces in
Adhesives Technology. In that practice it has been found that it doesn't
take more than a small population of these groups to be effective in improving
adhesive bonding.

The "one pass" sticking tendency on rods with 3M/777 tape was carried out on
3420 type drives by V. D. Harris and D. D. Larson using conditioned "sticking"
tapes. All the samples listed below were unsatisfactory:

- Electrodeposited chromium
- 60w/o Al₂O₃-40w/o TiO₂ (PFS)
- 50w/o Cr₂O₃-50w/o TiO₂ (PFS)
- 85w/o Al₂O₃-19w/o MgO-5w/o TiO₂ (PFS)
A porous surface of 87w/o Al₂O₃-13w/o TiO₂ with a lubricant of the perfluoralkyl polyether type rubbed onto the surface was temporarily satisfactory, indicating the role of lubrication. The test of a highly acidic surface of a refractory oxide, tantalum pentoxide (Ta₂O₅) (IEPS 0.5), is still to be done. It represents the best chance for resisting this tape's stick from a head surface point of view.

CONCLUSIONS/RECOMMENDATIONS
A rationale has been developed, though not completely validated to date, to guide practical management of chemical-physical interactions in a head tape interface system. It appears now that tailoring of head surfaces to account for tape deficiencies is possible but may not be practical in mixed tape library environments. However, the optimization of head-tape interfaces via interactive systems should be approached through consideration of chemical reactions designed to maintain surface characteristics (i.e. lubrication) essential for functional performance.

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