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 ½" 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 3M/777 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 ½" 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 $60^W/oAl_2O_3$ and $40^W/oTiO_2$ 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 per50-100$\overset{o}{A}^2$.

Additional H_2O surface layers.
Thickness depends on temperature and relative humidity.
Dots indicate hydrogen bonds

First H_2O surface layers tightly bound
Surface hydroxyl groups

Metal oxide layers.
Actual thickness and structure depend on metal substrate

Crystalline metal substrate

Key:
M - Metal Atom,   O - Oxygen, - O -   -OH,   O - H_2O
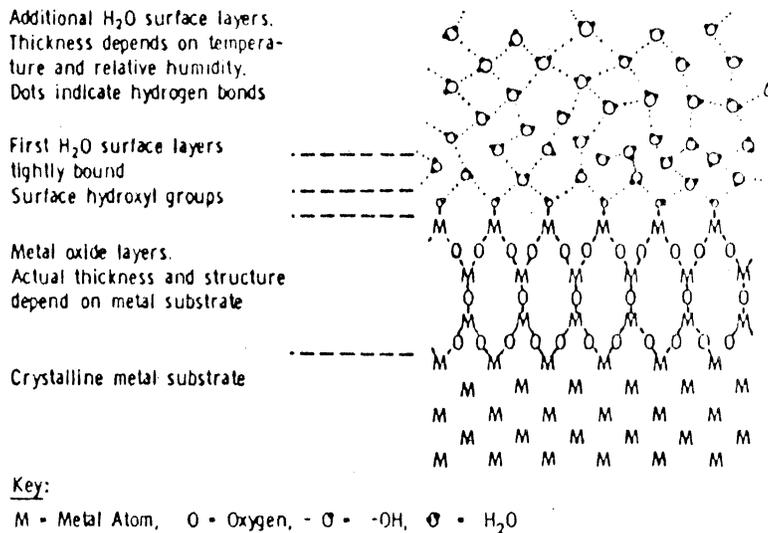
Fig. 1. Schematic representation of water and oxide layers on metal surface.

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:

$$-MOH + H_2O \longleftrightarrow -MO^- + H_3O^+$$
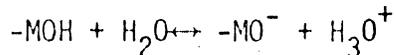
or via a (non-dissociative) adsorption process:

$$-MOH + OH^- \longleftrightarrow MOH \cdots OH^-$$
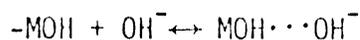
Similarly for a high electron density:

$$-MOH + H_2O \longleftrightarrow -MOH_2^+ + OH^- \quad \text{and}$$

$$-MOH + H_3O^+ \longleftrightarrow -M\overset{H}{O} \cdots H_3O^+$$
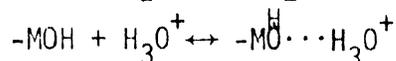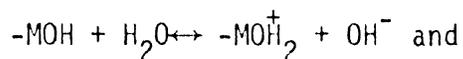
The equilibria for the above reactions depend both on the solid and on the electrolyte in which it is immersed. The surface charge can be calculated from Zeta potential measurements at various pH levels to determine the zero point of charge or isolectric point (IEPS) by using suspensions of powered samples 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[2] has found that the IEPS of an oxide can very 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.

$$IEPS = 18.6 - 11.5 \left[\frac{Z}{R}\right]_{eff}$$

Elemental Key:

A	- Mg	+ 2
B	- Fe	+ 2
C	- Co	+ 2
D	- Ni	+ 2
E	- Pb	+ 2
F	- Cd	+ 2
G	- La	+ 3
H	- Be	+ 2
I	- Cu	+ 2
J	- Zn	+ 2
K	- Y	+ 3
L	- Al	+ 3
M	- Th	+ 4
N	- Pu	+ 4
O	- Fe	+ 3
P	- Hg	+ 2
Q	- Ce	+ 4
R	- Zr	+ 4
S	- Cr	+ 3
T	- Ti	+ 4
U	- U	+ 4
W	- Sn	+ 4
X	- Mn	+ 4
Y	- Si	+ 4
Z	- W	+ 4

Key:
☐ HYDROXIDES AND HYDROUS OXIDES
◯ "ANHYDROUS" OXIDES - UNFLAGGED, CN-6
ρ CN-8   ◡ CN-4

$$\frac{Z}{R_{eff}} = \frac{CATION\ VALENCE}{EFFECTIVE\ CATION\ RADIUS}$$
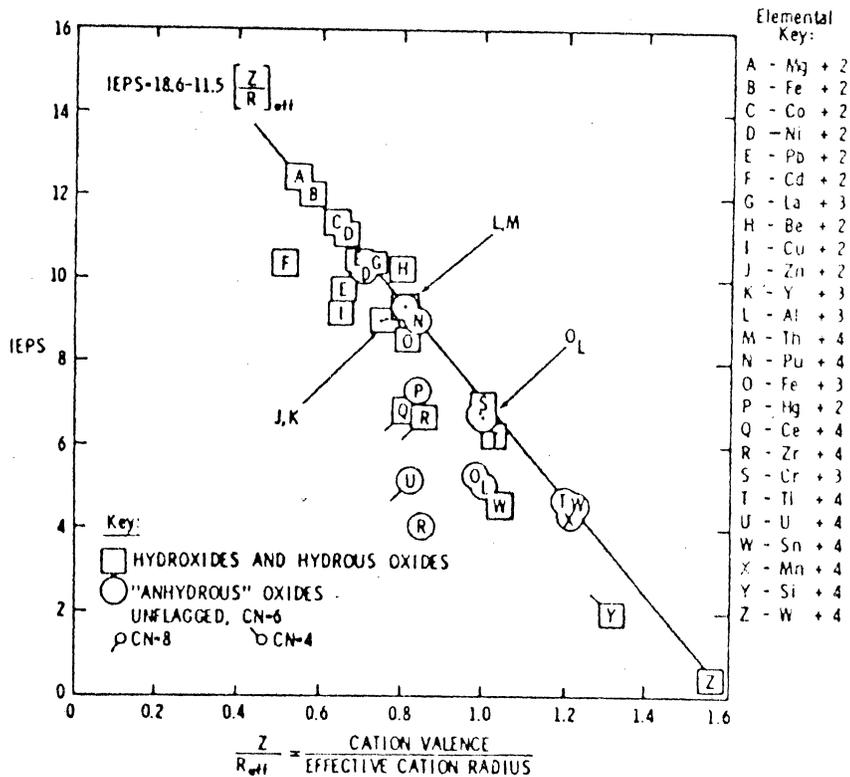
Fig. 2. Parks' equation for IEPS. Radius corrected for crystal field effects, coordination, and hydration

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:

$$A-H\cdots B \rightarrow A^-H^+-B$$
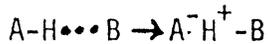
An oxide, for example, may interact with a carboxylic group to give either a dipole or an ionic bond:

$$-MOH + RC-OH$$

$$-MO\cdots HO-CR$$

$$-MOH_2^+\ ^-O-CR$$
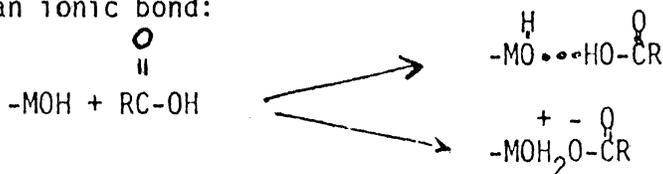
They have classified the possible interaction into two general interaction types. For type A, the surface provides the basic group which interacts with an organic acid. In type B, the surface provides the acidic group which inter-

acts with an organic base. Within each type they distinguish between two extreme conditions where the interaction is predominatly ionic or non-ionic:

A-1: Dipole interaction with organic acid

$$-MOH + HXR \rightarrow -M\overset{\cdot}{O}\bullet\bullet\bullet HXR$$

A-2: Ionic interaction with an organic acid

$$-MOH + HXR \rightarrow MO^{+}H_2\overset{-}{X}R$$
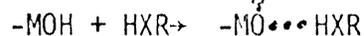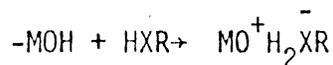
B-1: Dipole interaction with an organic base

$$-MOH + XR \rightarrow -MOH\bullet\bullet\bullet XR$$
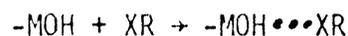
B-2: Ionic interaction with an organic base

$$-MOH + XR \rightarrow -MOH\overset{-}{X}\overset{+}{R}$$
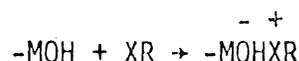
X is an electronegative atom usually oxygen or nitrogen. To predict the probability of an interaction for a given oxide surface - polar group combination, they derive a delta, Δ_A, Δ_B, for type A or B interactions which is related to the equilibrium constants for a polar group acid or conjugate base and the IEPS:

$$\Delta_A = IEPS - pKa(A)$$
$$\Delta_B = pKa(B) - IEPS$$

The qualitative relationship between the bond energy and Δ_A or Δ_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).
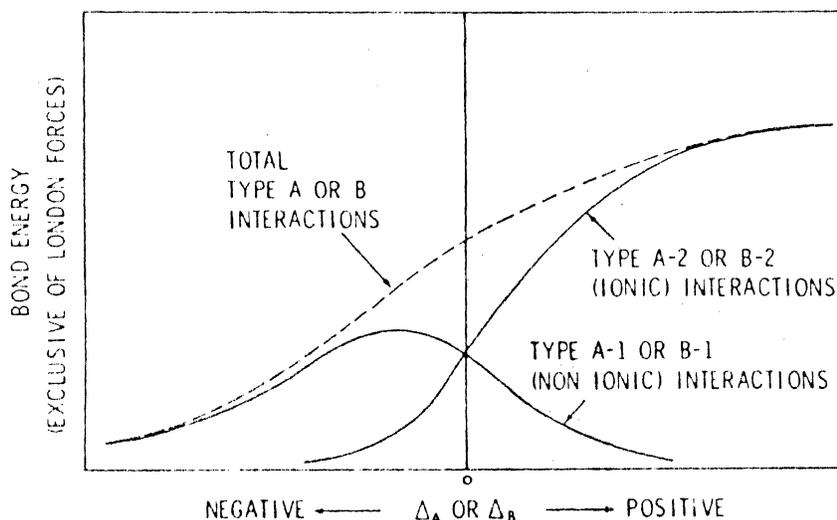
FIG. 3 Qualitative relationships between formation energy for electrostatic interactions and ionization parameters Δ_A or Δ_B.

Aliphatic Amines >> Carbox. Acids = Water > Alcohols , Phenol > Ketones
ΔB - 8 ΔA - -2.5 ΔB - -3 ΔB - -6 ΔA - -8 ΔB - -9

Carbox. Acids >> Phenol >> Amines > Water > Alcohols >> Ketones
ΔA - 7.5 ΔA - 2 ΔB - -2 ΔA - -3 ΔA - -4 ΔA - -8
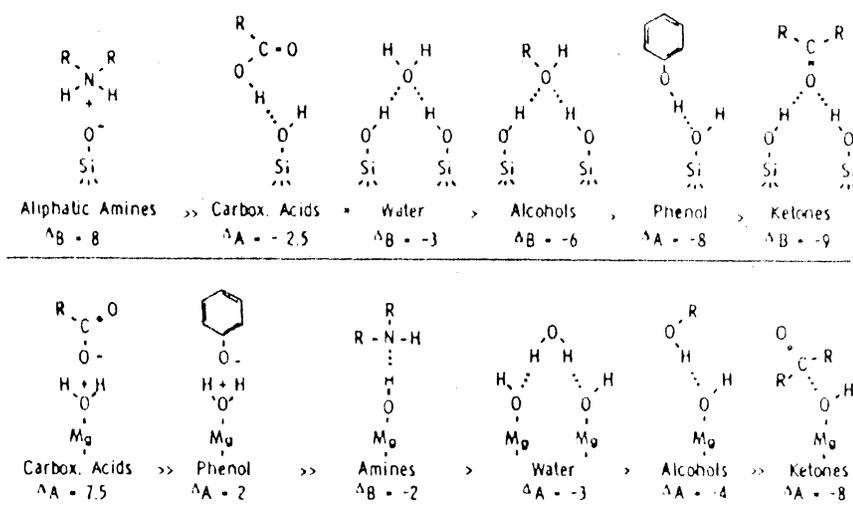
FIG. 4: Dipole orientations, dominant interaction modes, and relative bond strengths predicted for high IEPS surface (for example, MgO) and low IEPS surface (for example, SiO_2).

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 carbonyl 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:

$$\sim AlOH + R_3N \leftrightarrow AlOH \overset{-}{N}R_3^{+}$$

$$IEPS \geqslant 9 \qquad pKa_{(A)} \simeq 10, \quad \Delta_B = +1$$
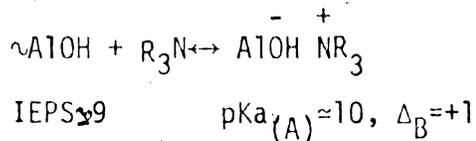
(Ionic interaction with an organic base)

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):

$$\sim NiOH + R_3N \leftrightarrow NiOH \cdots NR_3$$

$$IEPS \simeq 10.5 \qquad pKa_{(B)} \simeq 10, \qquad \Delta_B = -0.5$$
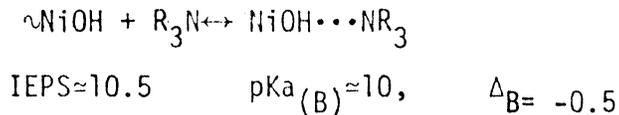
(Dipole interaction with an organic base)

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:

$$\sim AlOH + ROH \leftrightarrow AlOH \cdots OHR$$

$$IEPS \simeq 9 \qquad pKa_{(B)} \simeq -4 \qquad \Delta_B = -13$$
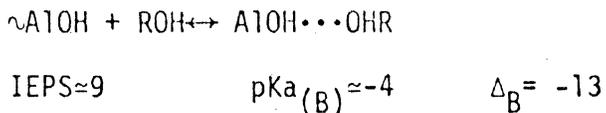
Thus, for an optimum solution to the S/500 problem of stick we need a basic surface; the more basic the better.

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

20μ" peak to valley to avoid "cow-catcher" effects. Similarly, only coatings whose wear rate was less than 100μ"/200 full reel passes are considered to avoid "abalative" effects though this point could be arguable on a micro-basis. Satisfactory qualitative results[5] were obtained on the plasma flame sprayed coatings following:

Al_2O_3

Cr_2O_3

$3Al_2O_3 \cdot 2SiO_2$ (Mullite)

$Al_2O_3 \cdot MgO$ (Spinel-Magnesium Aluminate)

85w/oAl_2O_3-10 w/o MgO-5 w/oTiO_2 (Composite plus blend)

87w/oAl_2O_3-13 w/o TiO_2 (composite powder - Metco #130)
70w/oAl_2O_3-30w/oTiO_2 (Blend - analyzed)

60w/oAl_2O_3-40 w/oTiO_2 (composite powder- Metco #131VF)

60w/oAl_2O_3-35 w/o MgO-5w/oTiO_2 (composite plus blend)
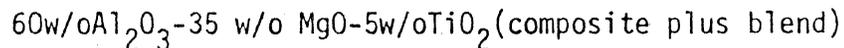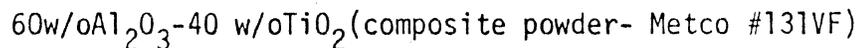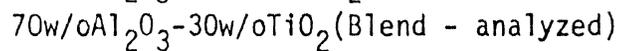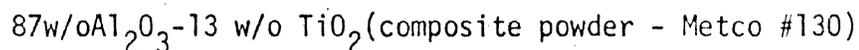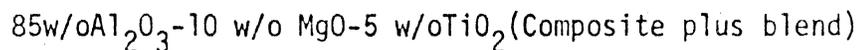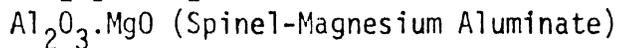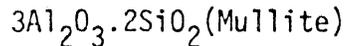
As the amount of a more basic oxide (i.e., MgO) was added to Al_2O_3 the results were somewhat better compared to those where more acidic oxides (TiO_2, SiO_2) were added. The 60w/oAl_2O_3-40w/oTiO_2 coating met requirements for manufacturability and head life.

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)
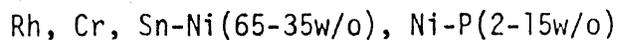
Sputter Deposited Coatings:

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/oAl_2O_3-50w/oTiO_2 (blend, sieved, analyzed)

Cr_2O_3+ Trace of Cr metal
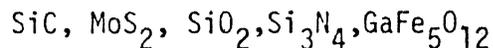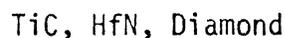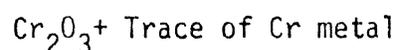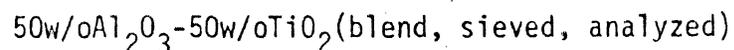
It is apparent that metals and alloys, carbides, borides, nitrides, silicides are unsatisfactory. Oxides as acidic as TiO_2 are also unsatisfactory. For

a mixture of Al_2O_3 and TiO_2 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 carboxlyic character and an alumina surface:

$$\sim AlOH + HO\overset{O}{\overset{\parallel}{C}}R \longleftrightarrow AlOH_2\overset{+}{}O\overset{-O}{\overset{\parallel}{C}}R$$
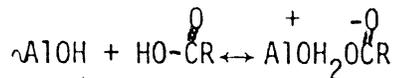
$$IEPS \cong 9 \qquad pKa(A) \cong 4.5 \quad , \quad \Delta_A = +4.5$$

(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 (WO_3) or tantalum pentoxide (Ta_2O_5):

$$WOH + HO\overset{O}{\overset{\parallel}{C}}R \longleftrightarrow WOH \cdots HO\overset{O}{\overset{\parallel}{C}}R$$
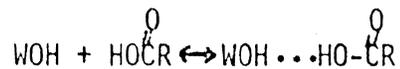
$$IEPS \cong 0.5 \qquad pKa(A) \cong 4.5 \quad , \quad \Delta_A = -4$$

(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 carboxy(-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/oAl_2O_3-40w/oTiO_2 (PFS)
> 50w/oCr_2O_3-50w/oTiO_2 (PFS)
>
> 85w/oAl_2O_3-19w/oMgO-5w/oTiO_2 (PFS)

TiO_2 (PFS)

$3Al_2O_3 \cdot 2SiO_2$ (Mullite-PFS)

TiB_2, TiC (PFS)

A porous surface of 87w/oAl_2O_3-13w/oTiO_2 with a lubricant of the perfluroalkyl 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 (Ta_2O_5) (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 manaement 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.

Acknowledgements

References

1) Bolger, J. C., and Michaels, A. S., "Molecular Structure and Electrostatic Interactions at Polymer-Solid Interfaces", Chapter I, pp. 1 - 60, "Interface Conversion", P. Weiss and D. Cheever, Editors Elsivier, 1969.

2) Parks, G. A., "The Isoelectric Points of Solid Oxides, Solid Hydroxides and Aqueous Hydroxo Complex Systems", Chem. Review 65, pp. 177-198, 1965.

3) F. S. deCormier, Private Communication

4) F. P. Curry, Private Communication

5) C. Meldrum, W. D. Kehr, R. Polleys - Technical Report to be published, 1974