Molecular Sieves and the Prevention of the "Vinegar Syndrome"

The following information was extracted from a paper that was presented at the 1992 AMIA Conference on December 10, 1992, by Dr. Tulsi Ram.

Cellulose triacetate or safety base completely replaced cellulose nitrate as the material used for motion picture film base by 1951-52, primarily because of flammability concerns. At that time, it was thought that acetate base was far less vulnerable than nitrate to long term decomposition and deterioration. And, while this is basically true, it wasn't until the 1980's that scientists began to understand the reactions surrounding acetate deterioration. This deterioration has become known as Vinegar Syndrome.

Cellulose triacetate is the product of a chemical reaction between cellulose and acetic acid. Vinegar syndrome is the reverse reaction of the breakdown of the acetate. This has been dubbed "deacetylation" and results from hydrolysis; the acetate ion reacts with moisture to form acetic acid. It's this acid that produces the characteristic vinegar odor. The mere presence of this odor does not mean the film in question has significantly deteriorated; but, it does mean the breakdown reaction is taking place. Excessive moisture and acetic acid are the prime catalysts for the reaction. Once started, the reaction produces more acid, becoming "autocatalytic". Once the reaction begins, it can't be stopped. In fact, it speeds itself up, growing faster and faster. Moreover, the acid produced can also react with dyes in color films, causing deterioration and damage to the image as well as the base.

Research personnel within EASTMAN Kodak Company recently announced Molecular Sieve technology which appears to be an effective deterrent to vinegar syndrome effects. The studies show that including a molecular sieve within the container used to archivally store film, combined with current recommended practices, can extend the life of the film far beyond what is now considered normal.

The type of molecular sieve selected for this application can adsorb moisture, acetic acid and, as a bonus, methylene chloride. The molecular sieve material is packaged in a packet made of spun-bonded polypropylene that enables the sieve to "breathe".

Again, the use of molecular sieves **should not** replace the current recommended long-term film storage practices. Test data accumulated thus far show that molecular sieves can become an easy, practical way to give **extra** protection and life to archivally stored film.

A technical paper describing Kodak's detailed experiments and results is currently being written for publication. In general, significant improvements in dye stability and a reduction of the vinegar syndrome reaction by using molecular sieves were observed. Gas chromatographic and mass spectral analysis detected the presence of acetic acid, methylene chloride, propylene dichloride, acetone, methanol, butanol and water after using molecular sieves. This means the sieves performed as they were expected. They absorbed the byproducts of the acetate decomposition and small amounts of residual

solvent used to manufacture the film. By scavenging the acids generated by the vinegar syndrome reaction, the molecular sieves greatly reduced the rate of reaction. This, in turn, improved dye stability because base deterioration produces acid which reduces dye stability.

Also tested were certain physical properties of the film samples to see what effect molecular sieve would have on film brittleness, viscosity, tensile strength, pitch shrinkage, etc.. In general, all these physical properties were better in the samples stored with molecular sieve.

The data generated from the experiments were obtained by evaluating incubated samples and using an Arrenhius extrapolation to estimate natural age keeping.

Kodak believes that including a molecular sieve in the can or packaging used to archivally store film can extend the life of the film support and the dye images far beyond what is now considered "normal" using recommended storage procedures. Work within the industry to gain additional experience and explore this new technology will continue. EASTMAN Kodak Company is confident that molecular sieves will prove to be an easy, practical way to give **extra** protection to archivally stored film.