FAILURES CAUSED BY ADDITIVES AND CONTAMINANTS DURING PROCESSING AND STORAGE

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1. Introduction

Additives are normally present in plastics formulations intentionally for a variety of purposes. There may also be unintentional additives, such as water, contaminants, and compounding process aids[1]. Both intentional and unintentional additives can have undesirable effects on product quality or cause failure during processing and storage of products. Examples are given below. In these examples, several different types of failure are represented. In some cases, the cause of failure was determined with the aid of plastics analysis, notably headspace GC/MS (gas chromatography/mass spectroscopy)[2,3] and micro infrared spectroscopy. Headspace GC/MS has been developed here as a prime method of analysis of formulations containing compounds sufficiently volatile to be transferred into a gas chromatograph at headspace temperatures up to 300-350°C. That includes many plasticizers, antioxidants, flame retardants, lubricants, etc.

2.0 Examples of failures

2.1 Polymer decomposition by acidic byproducts of flame retardants and of other additives formed in processing

2.1.1 Halogenated hyrodcarbon flame retardants containing chlorine or bromine may decompose, releasing small amounts of hydrogen chloride (HCl) or hydrogen bromide (HBr) during processing. This has caused polymer decomposition of insulation in electrical cables. One such case was thin Mylar PET film wrapped around the cable conductor, on top of which was peroxide-crosslinked EPR insulation containing a brominated flame retardant. The Mylar film was embrittled and fractured over a long length of cable on completion of processing. Bromine was detected in the degraded Mylar by SEM-EDX analysis. During crosslinking in steam under pressure, a small amount of HBr from the flame retardant was ionized to hydrobromic acid, causing hydrolysis of the polyester. Control of the problem requires the use of the lowest temperature that is adequate for effective crosslinking. A compound that would react with and neutralize the HBr as it forms may also be effective.

2.1.2 A similar cable formulation without Mylar was aged at 150°C in an air oven after processing to determine heat resistance. Surface brown spots formed which were brittle, i.e., cracked on flexing (figure 1). This effect was due to HBr evolved by flame retardant, which reacted with lead oxide and zinc oxide present. In the ionic state, lead, in particular, is a catalyst for oxidation of polyolefins. This experiment showed that HBr is evolved at low levels at 150°C, within the range used to crosslink cable polymers during processing (2.1.1 above).

2.2 Polymer decomposition by additives other than flame retardants

Embrittlement of Mylar film wrap, as in 2.1.1, took place also in a cable which contained toluenesulfonamide in an outer wrap of glass braid. The acid that caused hydrolysis of Mylar appears to have been toluenesulfonic acid, formed by hydrolysis of toluenesulfonamide. The toluenesulfonic acid dissolved in the aqueous steam curing medium, as in 2.1.1, and degraded Mylar. The presence of toluenesulfonamide was detected by headspace GC/MS. See 2.4.1 for experimental conditions.

In general, any component of the formulation that can generate a strong acid, or an acidic condition in the curing medium to which the cable is exposed during crosslinking, may cause hydrolysis of hydrolyzable materials such as amide compounds and ester polymers.

2.3 Environmental stress-cracking (ESC) by compounding process aids

White HDPE injection molded syringes for inoculation of cattle fractured while in storage after molding. An oily liquid had exuded to the surface and caused ESC. The liquid was identified as a phthalate plasticizer by infrared spectrscopy, and confirmed to be dibutyl phthalate (DBP) in legal testimony by the compounder. DBP had been used by the color concentrate compounder to wet the carrier resin pellets so that uniform dispersion would be facilitated. This is a common practice which will not contribute to failure as long as the product is not susceptible to stress-cracking or other problems if the process aid migrates to the surface. With HDPE, however, DBP is capable of causing stress- cracking. High crystallinity causes extraneous materials like DBP that cannot be accommodated in the crystalline polymer structure to be excluded and, in time, to migrate to the surface. In litigation that followed, the compounder admitted using DBP, but an "expert witness" incorrectly claimed that it would not cause polyethylene to fracture. Other problems that have been caused by compounding process aids include low adhesion, due to migration of materials such as zinc stearate to the surface of coextruded polyolefin film. Lubricants used to prevent sticking during molding or extrusion have also interfered with adhesion in other cases.

2.4 Localized adhesive failure between two coatings

The inner lining and seal of bottle caps used in beverage containers consisted of a thin metal base onto which a phenolic epoxy primer coat was deposited. The topcoat was plasticized vinyl. Localized delamination of the topcoat, ca. 1-2 mm^2, occurred on a small percent of the area, as a result of installation of the liners in the caps. It could also be duplicated by removing adhesive tape. A possible cause of low adhesion was incompletely removed lubricant used during manufacture of the metal sheet prior to any coating operations. That was shown not be a factor in two ways: (1) adhesive failure was at the interface

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[1] M. Ezrin, "Case Studies of Failures Due to Unintentional Service Conditions", SPE ANTEC, 1991, Montreal, 2213-2216.

[2] M. Ezrin and G. Lavigne, "Failure Analysis Using Gas Chromatography/Mass Spectroscopy", SPE ANTEC, 1991, Montreal, 2230-2233.

[3] M. Ezrin and G. Lavigne, "Application of Direct Dynamic Headspace GC/MS to Plastics Compositional and Failure Analysis", SPE ANTEC, 1992, Detroit, 1717-1719.

between the primer and the topcoat, not between the metal and the primer; (2) analysis by headspace GC/MS showed the complete absence of lubricant, even using single ion monitoring by the mass spectrometer.

The surface of primer where topcoat had lost adhesion was examined by micro infrared spectroscopy, microscopy, and headspace GC/MS. By microscopy a locus of failure could be observed (figure 2, top center). In the original colored photo, a circular oil-like stain surrounds the locus. In some cases, a very fine lint fiber could be seen, and infrared gave a typical cellulose spectrum. In other cases, the locus of adhesive failure appeared to be a mechanical defect in the metal, such as a very small indentation. Generally, a tiny droplet of oily liquid could be seen (figure 3). In the colored original microphoto at 1000 X mag., well-defined colored intereference fringes could be seen emanating from two black lines (the locus of adhesive failure). In the black and white photo of figure 3, the interference fringes are seen as alternate light and dark lines. This phenomenon is a well-known indication of a substance on a surface with variable film thickness.[4] From the number of color fringes, the film thickness is estimated up to 1.5-2 microns. In the case of figures 2 and 3, there is no well-defined contaminant such as a fiber. It may have been removed along with the topcoat when it separated from the primer. Figure 3 also shows seperate tiny globules of oil (lower right).

Micro IR of the liquid was not sensitive enough nor had sufficient resolution to identify the liquid. Headspace GC/MS, however, was very informative about composition at the surface where topcoat had been removed due to low adhesion (1), relative to surface with normal adhesion from which the topcoat was scraped off with a razor blade (2). In the former case (1), the content of certain plasticizer and other volatile materials in the primer and topcoat was significantly higher than at the surface from which the topcoat had been scraped off. There had been extensive exchange of plasticizer and other nonpolymeric components between the primer and the topcoat. DOP plasticizer was identified, as well as fatty acid esters, squalene and cholesterol. These did not significantly reduce adhesion between the two coatings, where they are tightly in contact. But, where a contaminant was present between primer and topcoat, so that adhesion was less than normal at that point, some liquid undergoing transfer between layers accumulated at the contaminant site. That is what was observed by microscopy (figure 3). With the accumulation of oily liquid compounds at contaminant sites, over time, adhesion at these sites became so low that topcoat was easily removed.

Figure 4 is a chromatogram for a combination of the metal, primer and the bare surface from which topcoat had been lost due to poor adhesion; figure 5 is the same for an area from which topcoat had been scraped as a control for figure 4. These chromatograms show significantly higher content in particular of squalene and fatty acid esters in the adhesive failure area. The source of squalene as well as cholesterol is unknown. However, the identification of squalene was confirmed by a reference mass spectrum and it was also possible by infrared spectroscopy to see sufficient characteristics of the infrared spectrum of squalene to help support squalene as the material. Squalene was also confirmed by the GC retention time with a reference sample. Cholesterol and fatty acid esters could be from epoxidized soybean oil believed to be a component of either or both of the primer and the topcoat. The identification by mass spectra of cholesterol and fatty acid esters, as well as of DOP plasticizer and squalene is certain. In other GC runs, another plasticizer from the vinyl topcoat was detected as dicyclohexyl phthalate. This is not seen as a separate peak in figures 4 and 5 because of the low content of the dicyclohexyl plasticizer.

The solution to this problem seems to be to prevent mechanical damage and contamination of the surface between primer and topcoat by lint and other materials that reduce the strength of the adhesive bond. Presumably a coating, such as EVA (ethylene vinyl acetate), without a high content of plasticizer and other liquid components would be less likely to lose adhesion.

2.4.1 Experimental Conditions of GC/MS, IR and Microphotography

Micro IR was done with a Spectratech unit in reflectance mode, using a Nicolet 60SX FTIR. For GC/MS with the direct dynamic headspace accessory[2,3], heating was 2 min. at 300° . Samples consisted of the metal, primer and surface material between primer and topcoat, and weighed ca. 1.6 mg. The weight of sample without metal is estimated at 0.1-0.3 mg. The GC column by H/P was 10 meters, 100% methyl silicone, 0.2μ film thickness, 0.2 mm ID, and the temperature program following headspace heating was 35° to 325° at 15° C/min. The mass spectra are by electron impact (EI) and the Y axis of the chromatograms is total ions. In Fig. 4 and 5 peak areas have been normalized to area/mg. sample to take care of sample weight differences. The spectrometer range (m/e) is 10-400. The microphotographs were taken with a Polaroid Microcam mounted on the micro IR.

2.5 Exudation of plasticizer of PVC tubing caused by pressure from the packaging

A DOP-plasticized PVC catheter (3/8 in diameter, 18 in. long) exuded plasticizer drops on the inside at one end of the tubing inside the package. The exudation was caused by storage with the end that exuded plasticizer pressed hard against the transparent package film (figure 6). Compatibility of plasticizer with PVC is reduced by pressure and is the basis of an ASTM test for compatibility (D3291). Because of the exudation the catheters could not be sold in that condition. Figure 7 shows that drops of DOP are more numerous toward the end where pressure against the packaging film was greatest(right). DOP was identified by infrared and by headspace GC/MS. The pressure also permanently deformed the round end of the tubing into an oblong shape (Fig. 6).

2.6 Undesirable effects of additives in molding operations.

These effects include those of intentional as well an unintentional additives, and have been experienced with mold release agents and antioxidants, among others. In the former case, deposits on mold surfaces have been a problem. With some antioxidants, plugging of vacuum vents has necessitated frequent cleaning of the vents. The mold deposit problem appears to be associated with stearic acid, for example, an unintentional additive present in calcium stearate (an intentional additive). Vent plugging has occurred with antioxidants sufficiently volatile to be picked up in the vent system, which condensed in the vents, causing plugging. In cases where vent deposit was collected and analyzed, it confirmed predictions based on GC/MS of the whole formulation. Another case of unintentional additive is vent plugging by caprolactam monomer in recycled nylon, in which the caprolactam content was high enough to cause plugging of vents.

2.7 Summary and Conclusions

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4. F.A. Jenkins and H.E. White, "Fundamentals of Optics", 3rd. ed., 1957, McGraw-Hill, Chapter 14, "Interference Involving Multiple Reflections", 261.

The cases cited above are only a small sample of varied unlikely failures, that have been experienced due to material present intentionally or unintentionally, as a result of thermal, hydrolytic or high stress conditions during processing and storage. One must be alert to such possibilities in formulating and processing plastics. Frequently the connection between the failure and the cause is not obvious. The analytical methods utilized in this paper (micro IR, microphotography, SEM/EDX (electron microscopy/elemental analysis) and headspace GC/MS) are some that can be helpful in determining the cause of failure.

The adhesion case in 2.4 illustrates how severely adhesion can be affected by trace contaminants and surface defects which cause liquid components, that are otherwise not a problem, to accumulate at localized sites. This is one of several cases in which squalene has been detected. Its origin and reason for its presence, intentional or unintentional, are not known for any of the several cases in which it has been detected.

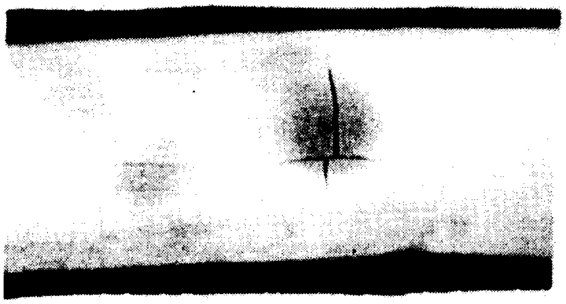

Fig. 1. Cracks formed on flexing surface brown spot of EPR insulation containing brominated hydrocarbon flame retardant, resulting from oven aging at 150° C.

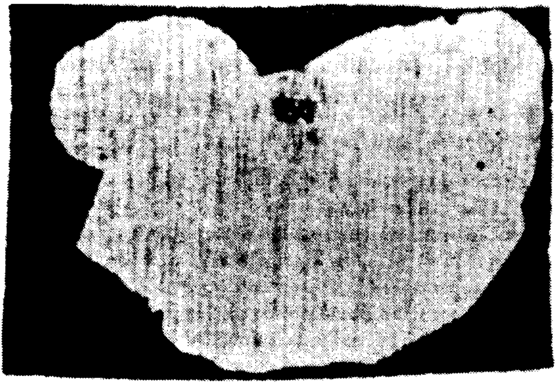

Fig. 2. Surface of primer coat on metal backing of cap liner, where topcoat was removed due to localized adhesive failure; locus of failure top center. Approx. 25X mag.

Fig. 3. Locus of failure of Fig. 2. Interference fringes of alternate dark and light lines due to liquid on the surface. Approx. 500X mag.

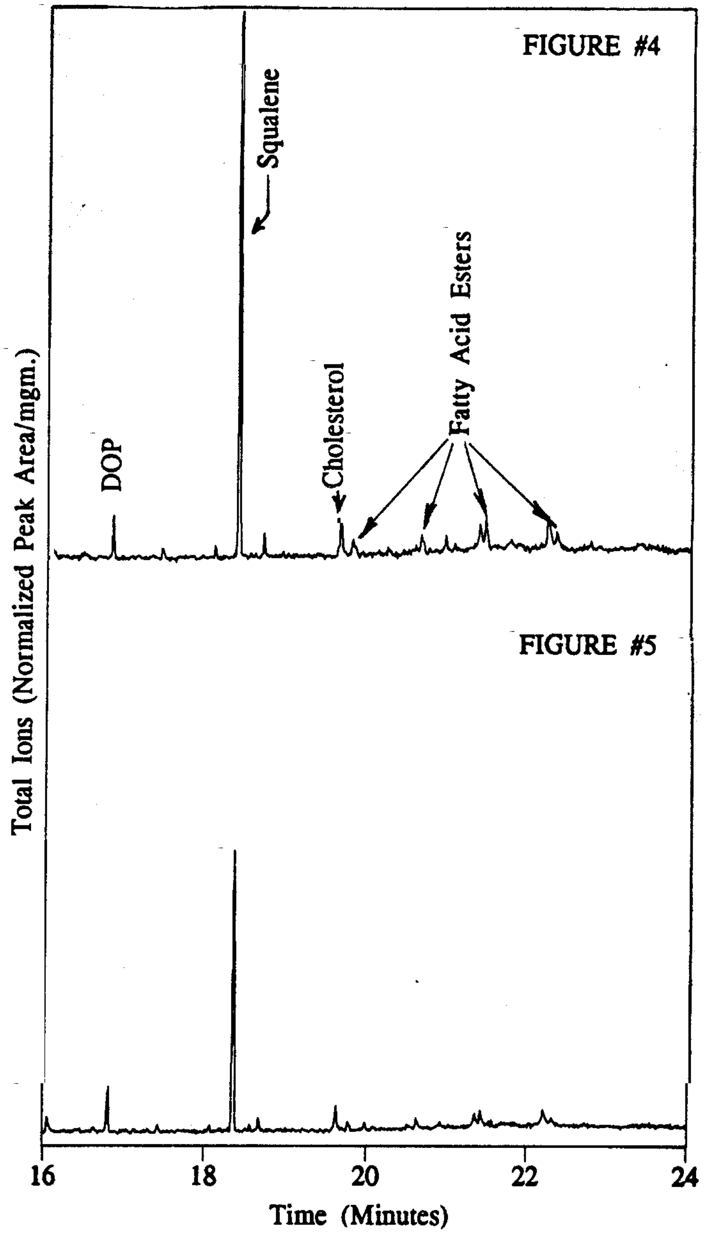

Fig. 4. Portion of headspace GC/MS chromatogram of metal plus primer from which topcoat was lost due to adhesive failure (Fig. 2,3). Fig. 5. Control for Fig. 4 - metal plus primer from which topcoat was scraped off at a location with normal adhesion of topcoat to primer.

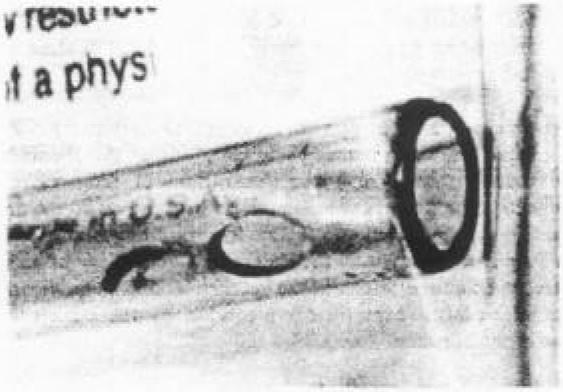

Fig. 6. End of DOP-plasticized PVC catheter under pressure inside clear packaging film in storage several months.

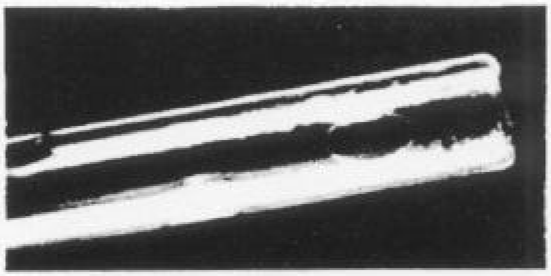

Fig. 7. Tubing of Fig. 6 with DOP drops (right) that exuded on inside surface due to pressure of the packaging in long-term storage.