EXTRUSION COATING

# Volatile organic compounds in LDPE films and air during extrusion coating

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## ABSTRACT

*During polyethylene extrusion processing, large amounts of unpleasant odors develop. LDPE lined aluminum cast film samples were made at two different extrusion temperatures to identify the VOCs formed during processing to the inner layer of test pouches of cardboard/aluminum/polyethylene laminate. A specially treated extrusion coating sample was analyzed to study the ability of an additive to reduce off-flavors. During extrusion coating, considerable volatile decomposition products spread into the surrounding air. VOCs and offensive odor compounds in the extrusion coating samples and air were studied using integrated sensory and analytical methods. Sample analysis used gas chromatograph/mass spectrometer methods.*

***Application:***

*Extrusion coating conditions play important roles in control of odor producing VOCs.*

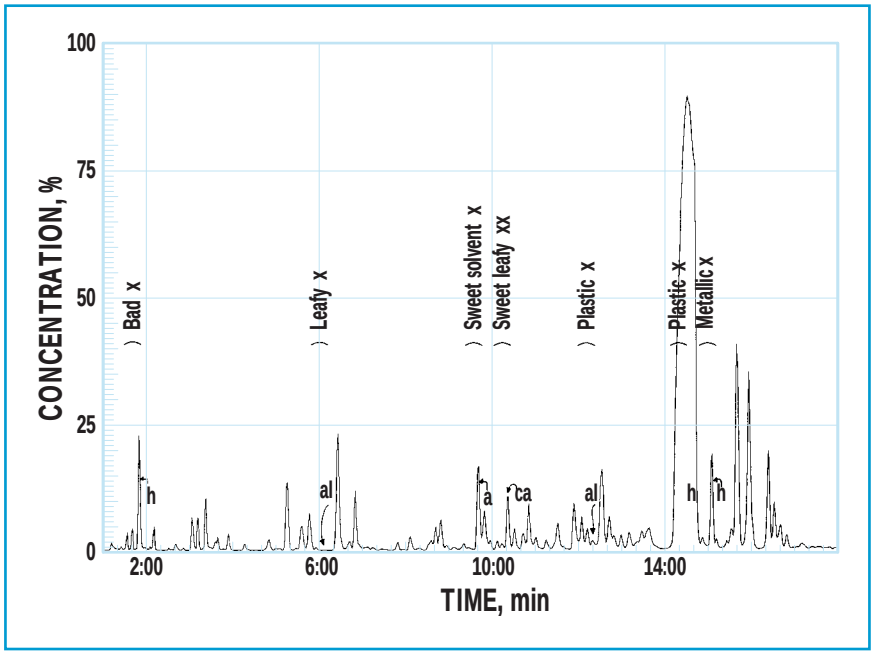

IN PLASTIC PACKAGING, QUALITY IS AN important issue. This includes the organoleptic properties of odor and taste. Interactions among the package, packed foods, flavor compounds, and polyolefins are major concerns *(1, 2)*. Using plastic films for food packaging can cause off-flavor problems due to residual additives and solvents *(3)*. Compounds that cause off-tastes and off-odors can also migrate into foods. Several studies have shown that chemical species can cause these off-flavors and indicated how the compounds form *(3–7)*.

Offensive odors and tastes primarily relate to volatile organic compounds (VOC). Carbonyl groups such as aldehydes, ketones, and carboxylic acids are especially responsible for a plastic flavor *(5)*. The carbonyl compounds form during extrusion to the inner layer of cardboard/aluminum/polyethylene laminates. The lamination of aluminum to polyethene eliminates the effect of the paper/cardboard usually used as a substrate on off-flavor formation *(8)*. Off-odors in polyolefins also can result from aromatic hydrocarbons *(9, 10)*. Most compounds identified in polyolefins are hydrocarbons—alkanes and alkenes—that have high odor threshold concentrations. These compounds are weak odor substances *(7)*. Saturated alkanes are organoleptically neutral compared with organic acids or aldehydes with equal carbon numbers *(2)*. Organic acids can influence odors due to their low vapor pressures when dissolved in water.

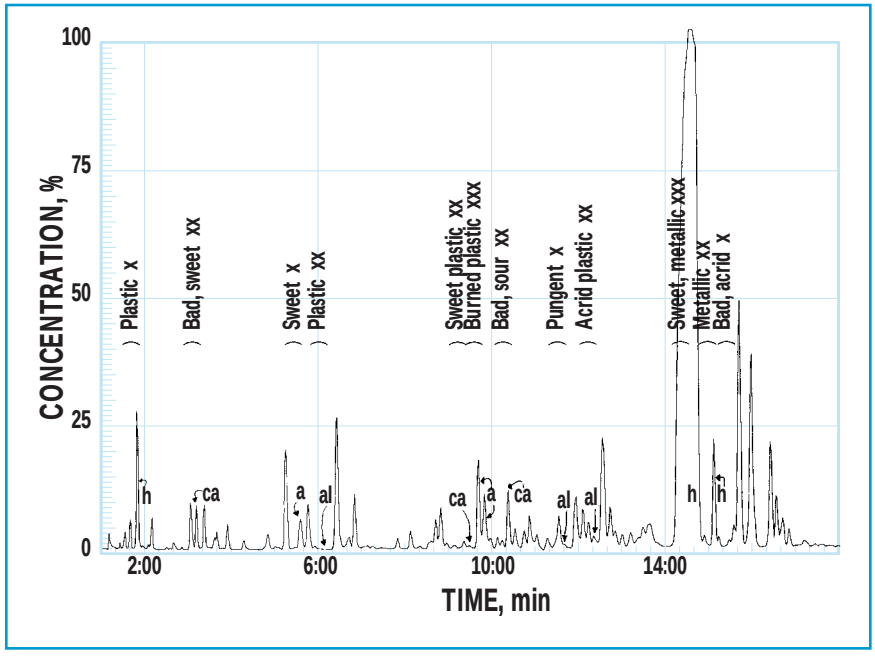
Kuijik *et al.* studied the compounds released from film samples into water and found aldehydes and ketones but no acids. The acids were below their detection limits due to their solubility in water *(2)*. Koszinowski *et al.* proposed that a single chemical compound or a mixture of several substances can produce off-odors. He also noted the difficulties in describing an odor caused by changes in the relative concentrations of different components in mixtures *(7)*. The odor threshold of a combination of components may be lower than the odor threshold values of the individual components. Some components may influence the total odor of packaged water even when their individual concentrations are low compared with their odor thresholds *(2)*.

Odors develop during film extrusion at high temperature. Hoff suggested that development of VOC during the processing depends on temperature and behavior of oxygen *(11)*. In the extrusion coating process, the processing temperature for the resin is usually 200°C–320°C *(12–14)*. When polyethylene is at these high temperatures in the presence of oxygen, the hydrocarbons form aldehydes, ketones, and carboxylic acids *(12)*. Wyatt showed the effect of different processing temperatures on volatile materials in two polypropylene samples. The gas chromatographic profiles of both samples were very similar. The differences were in the amounts of volatiles *(13)*. Brodie showed that the resin melt temperature used in the extrusion coating process is the main reason for off-taste. Higher extrusion temperatures give greater off- tastes *(14)*.

Good adhesion is necessary in many applications of polyolefins *(4)*. Although high temperatures form odor bearing groups in LDPE extrusion coating, oxidation is necessary for film adhesion to the substrate *(15)*. The best adhesion results from high oxidation because of the increase in polarity of the film surface. Polyethylene is normally nonpolar. After oxidation, it becomes polar. Coating grades of polyethylene do not usually contain additives *(8)*. In LDPE extrusion coating, antioxidant is unnecessary precisely because of the need for adhesion. In a review of the impact of vitamin E on adhesion, Zambetti showed that higher amounts of this antioxidant gave weaker adhesion *(15)*.




*1. Total ion chromatogram of the film sample 280A with odors and odor-causing compounds coded as ca = carbonyl compound, a = aromatic compound, al = alcohol, and h = hydrocarbon*




*2. Total ion chromatogram of the film sample 320A with odors and odor-causing compounds coded as in Fig. 1*

LDPE film extruded at high processing temperatures also emits many volatile decomposition products. Some have potential health hazards associated with overexposure. Tikuisis *et al.* studied the exposure of workers in commercial polyethylene extrusion operations and measured the airborne concentrations of emitted compounds *(12)*.

In this study, the authors report the off-flavor compounds in films and volatilized compounds formed during processing that can enter the air.

## EXPERIMENTAL

### *GC/MS analysis*

The gas chromatographic/mass spectrometric (GC/MS) analysis used a Hewlett-Packard gas chromatograph model 5890 Series II mass spectrometer with VG AutoSpec high resolution. The electron ionization (EI) potential was 70 eV. The column used in this analysis was Noribond SE 54 with 0.25 mm internal diameter, 25 m length, and 1 µm phase. The GC/MS system used two identical columns. One column led to the MS, and the other led to the funnel used for simultaneous sniffing *(16)*. Introducing the extrusion coating samples to the GC/MS used the purge and trap technique (Tekmar 2000). The purge gas was 99.995% pure helium with a flow rate of 40 mL/min. The lines for this equipment were at 100°C, and the temperature of the mount was 40°C. Operating conditions were a purge time of 12 min., sample temperature of 100°C, and injection temperature of 250°C. The oven program for GC was 5 min. at 40°C–5°C/min to 150°C–20°C/min to a final temperature of 250°C.

In the analysis of air samples taken during LDPE extrusion, the VOC were thermally desorbed from adsorption tubes into a GC/MS/sniff system. The principle of the thermal desorption/cold trap method is to heat the block while the carrier gas flows through the sample tube and desorbs the volatile compounds. Desorption temperature was 120°C, and the flow rate of the desorption gas was 1 mL/min. The desorption time was 10 min. Veijanen has presented a more detailed description of this thermal desorption/cold trap system *(17)*.

Using sniffing, the interpretation of the mass spectra of extrusion coating samples and air samples focused on the offensive smelling compounds.

### *Extrusion coating samples*

LDPE films used extrusion tempera-

| Compound | 280A odor description | 280A conc., mg/m$^3$ | 320A odor description | 320A conc., mg/m$^3$ | 320B odor description | 320B conc., mg/m$^3$ |
|---|---|---|---|---|---|---|
| Hexane (h) | Bad x | 2.8 | Plastic x | 3.5 | - | 1.9 |
| $C_8$ ketone (ca) | - | - | Bad, sweet xx | 0.3 | - | 0.02 |
| Toluene (a) | - | - | Sweet, x | 0.3 | - | - |
| 2-Hepten-4-ol (al) | Leafy x | 0.01 | Plastic xx | 0.01 | - | - |
| 2-Methyl-2-heptenal (ca) | - | 0.3 | Sweet plastic xx | 1.0 | - | 0.20 |
| *O*-xylene (a) | Sweet, solvent x | 0.06 | Burned plastic xxx | 0.07 | - | - |
| *P*-xylene (a) | - | - | - | 1.6 | - | - |
| 4-Octen-3-one (ca) | Sweet, leafy x | 0.6 | Bad, sour xs | 0.6 | - | 0.10 |
| $C_7$ alcohol (al) | - | - | Pungent | 0.01 | - | 0.01 |
| $C_7$ alcohol (al) | Plastic x | 0.8 | Acrid, plastic xx | 0.9 | - | - |
| 2,2,4,6,6-penta-methylheptane (h) | Plastic x | 9.5 | Sweet, metallic xxx | 16.3 | Plastic x | 11.8 |
| 2,2,7,7-tetra-methyloctane (h) | Metallic x | 2.0 | Metallic xx | 3.2 | Burned plastic x | 2.5 |
| $C_9$ alcohol (al) | - | 0.4 | Bad, acrid x | 0.5 | - | 0.5 |

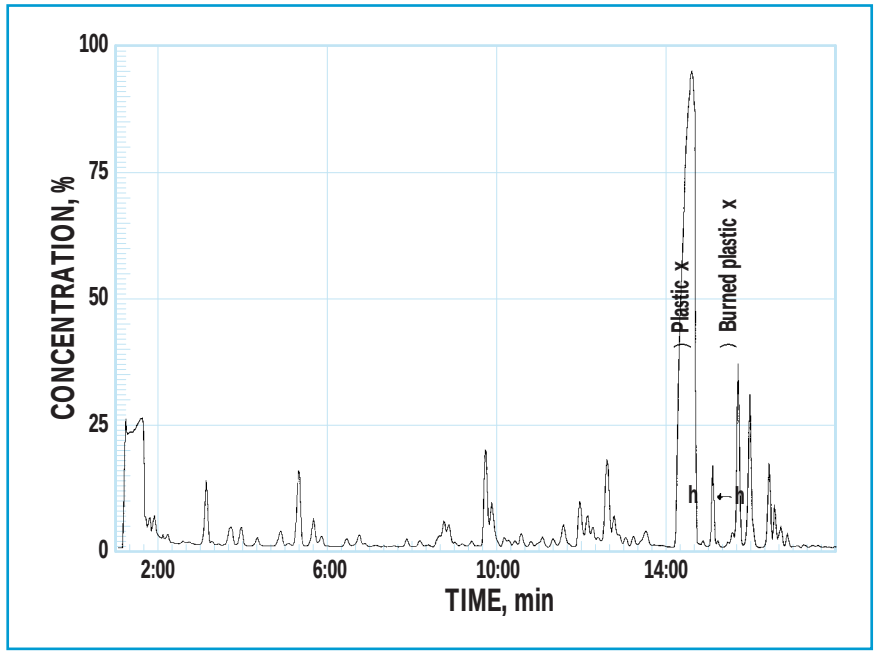
***I. Odor descriptions and concentrations in mg/m$^3$ of off-flavor compounds in extrusion film samples 280A, 320A, and 320B with parenthetical expressions the same as Figs. 1–3 (x = weak odor, xx = moderate odor, xxx = strong odor, and xxxx = very strong odor)***

tures of 280°C and 320°C. Two samples were made at 320°C, and one sample was made at 280°C. These film samples had designations 280A, 320A, and 320B. The 320B had a special treatment with an additive. 2.5 g of each extrusion coating sample was cut into pieces and put into the purge and trap vessel (25 mL). The GC/MS/sniff analyzed the volatile, offensive smelling compounds using purge and trap equipment.

### *Air samples*

The air samples were collected with an air pump from air over molten resin near the extruder using filled adsorbent tubes. The matrix is poly-*p*-2, 6-diphenylphenylene oxide with 23% graphite.

The amount of adsorbent in a glass tube was 225 mg. These sample tubes were thermally cleaned before sampling and stored in a sealed vessel under pressure. In the cleaning, the tubes were at 320°C for at least 6 h in a purified nitrogen flow (20 mL/min.). The processing air samples were drawn through the sample tubes with a flow rate of 100 mL/min. (calibrated air pump SKS Model 222–3). The volumes of collected air samples near the extruder were 3 L for 280°C and 2 L for 320°C. Analysis of a blank sample tube provided knowledge of the normal background. This tube underwent the same handling procedures as the real samples.




***3. Total ion chromatogram of the film sample 320B with odors and odor-causing compounds coded as in Fig. 1***

## RESULTS AND DISCUSSION

### *Extrusion coating samples*

The film samples primarily gave peaks showing alkanes and alkenes—branched or linear. Hydrocarbons with oxygen containing functional groups are an important class of odor-active compounds. In these samples, odor causing compounds were alkylbenzenes, alcohols, carbonyl compounds such as aldehydes and ketones, and hydrocarbons—branched alkanes with high molecular weight. **Figures 1–3** show the chromatograms with odors and intensities from three extrusion coating samples. **Table I** shows the identities of the odor causing compounds.

As Figs. 1–3 and Table I show, the amounts of off-odors increased considerably when extruding sample at 320°C. Note that odors decreased with the special additive—sample 320B. Carbonyl compounds like ketones and the aldehyde, 2-methyl-2-heptenal, were present in high

| Compound | 280 odor description | 280 conc., mg/m³ | 320 odor description | 320 conc., mg/m³ | TOC mg/m³ |
|---|---|---|---|---|---|
| 2-Butenal | - | <0.01 | Sweet x | <0.01 | 0.389 |
| Butanal | Sweet x | 0.02 | Sour xxx | 0.03 | 0.028 |
| 2-Pentenal | - | <0.01 | - | - | - |
| 2-Ethyl-2-butenal | Acrid xx | <0.01 | - | - | - |
| Hexanal | Leafy xxx | 0.01 | Leafy xxx | 0.10 | 0.058 |
| Heptanal | Aldehydic xxx | 0.05 | Dirty, leafy xxxx | 0.10 | 0.028 |
| Octanal | Aldehydic xxx | 0.05 | Bad, acrid xxxx | 0.12 | 0.007 |
| Nonanal | Dirty xxx | 0.01 | Acrid, dirty xxx | 0.01 | 0.014 |
| Decanal | - | 0.03 | - | 0.10 | 0.006 |
| Undecanal | - | 0.03 | - | 0.07 | 0.012 |
| Total aldehydes | | 0.20 | | 0.53 | |
| Acetic acid | Acetic xx | <0.01 | Acetic xxx | <0.01 | 0.363 |
| Propanoic acid | Dirty, bad xx | 0.01 | Dirty xx | 0.01 | 0.110 |
| Butanoic acid | Unpleasant xxxx | 0.02 | Unpleasant xxxx | 0.05 | 0.014 |
| Pentanoic acid | - | 0.01 | Plastic x | 0.03 | 0.024 |
| Hexanoic acid | - | <0.01 | - | 0.02 | 0.060 |
| Heptanoic acid | - | 0.02 | - | 0.02 | 0.148 |
| Octanoic acid | - | <0.01 | - | <0.01 | 0.024 |
| Nonanoic acid | - | - | - | <0.01 | 0.013 |
| Total carboxylic acids | | 0.06 | | 0.13 | |
| Methylcyclohexanone | - | <0.01 | - | - | - |
| MIBK | Pungent xxx | <0.01 | Bad, plastic xx | <0.01 | 2.19 |
| 3,4-dimethyl-cyclopentanone | - | <0.01 | Sweet, plastic xx | 0.06 | - |
| Ethylcyclohexanone | - | - | Bad, pungent xx | 0.01 | - |
| 7-Octen-2-one | Dirty, plastic xx | 0.04 | Unpleasant xxx | 0.05 | - |
| 4-Decanone | Sweet xx | 0.04 | Dirty, plastic xx | 0.03 | - |
| 5-Decanone | - | - | Spicy xx | 0.03 | - |
| 2-Decanone | Sweet xx | 0.02 | Dirty, acrid xx | 0.02 | 0.053 |
| 5-Undecanone | Plastic x | <0.01 | - | 0.01 | - |
| Undecanone | - | <0.01 | - | 0.01 | 0.155 |
| Total ketones | | 0.10 | | 0.22 | |

***II. Odor descriptions and concentrations in mg/m³ of odor causing compounds in the air samples collected at extrusion temperatures of 280°C and 320°C***

concentrations especially in sample 320A. They caused unpleasant odors with high intensities. Using the additive in Sample 320B, the carbonyl compounds disappeared.

The large peak in chromatograms of all three extrusion coating samples at 14.30 min. was due to 2,2,4,6,6-pentamethylheptane (PMH). The amount and odor intensity were greatest in film sample 320A. The odor description of PMH was sweet and metallic in sample 320A, but the description was weak and plastic in the other two extrusion coating samples. Most identified hydrocarbons caused no odors. Hexane had a weak, bad, and plastic-like odor. The 2,2,7,7-tetramethyloctane gave a metallic odor in 280A, a metallic odor in 320A, and a burned plastic odor in 320B.

The strongest odor in extrusion coating sample 320A came from *o*-xylene (1,2-dimethylbenzene) with a strong, burned-plastic odor. This off-flavor compound also caused a sweet, solvent odor in extrusion coating sample 280A with a weaker intensity. In sample 320B, the odor did not occur.

Some alcohols caused off-odors in film samples, although most only appeared in sample 320A. The one identified in all three extrusion coating samples was 2-hepten-4-ol. Its odor description varied with extrusion temperature. In sample 280A, the odor was weak and leafy. In sample 320A, it was plastic-like. The description was weak and metallic in extrusion coating sample 320B. The amount of this alcohol was greatest in film sample 320A.

### *Air samples*

Air samples were collected from molten resin near the extruder when extrusion temperatures were 280°C and 320°C. Odor producing compounds were carbonyl compounds such as aldehydes, ketones, and carboxylic acids. The compounds appearing in both air samples were primarily hydrocarbons—alkanes and alkenes. The total amount of hydrocarbons was larger when the extrusion temperature was 280°C. The total quantity of carbonyl compounds was higher at an extrusion temperature of 320°C. **Table II** and **Figure 4** show the amounts of all carbonyl compounds found in the air samples. Table II also identifies the odor descriptions of the

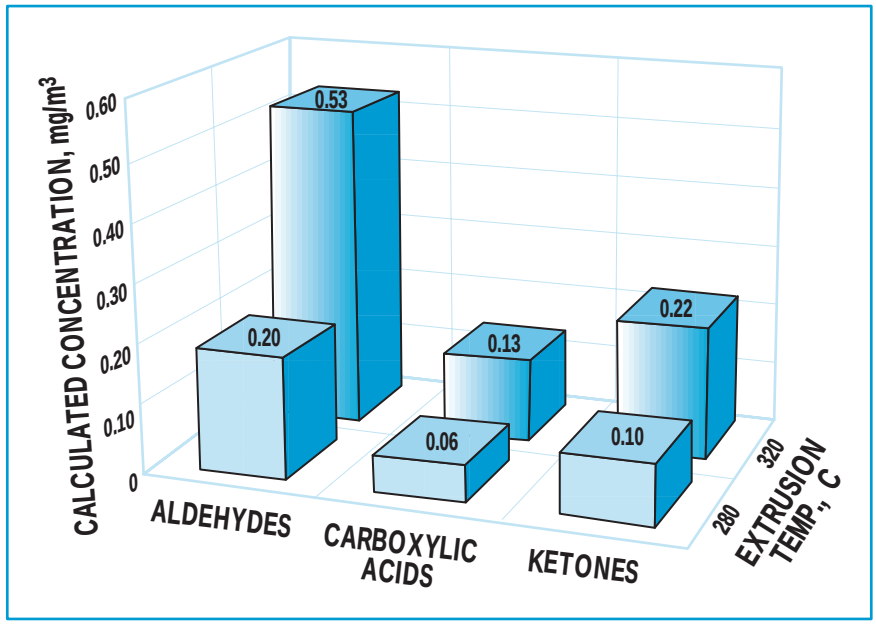
KEYWORDS
*Air, air pollution, aluminum, extrusion coating, flavor, food, low density polyethylene, odor control, odors, packaging films, pollution control, samples, taste, test methods, VOC.*

offensive smelling compounds.

The concentrations of most aldehydes exceeded the threshold odor concentrations (TOC) especially in the air sample collected during 320°C extrusion. Heptanal caused the strongest odor of aldehydes. Its odor description was dirty and leafy. Most descriptions were unpleasant with high intensity. 2- pentenal and 2-ethyl-2 butenal (acrid odor) appeared only in the air sample collected during extrusion at 280°C. 2-butenal with a weak, sweet odor occurred only in the sample collected with extrusion temperature at 320°C. The total concentration of identified aldehydes was much higher at 0.53 ppm in the air sample collected at 320°C compared with the air sample taken 280°C—0.20 ppm.

Carboxylic acids occurred in both air samples and caused bad, unpleasant odors. The carboxylic acids with low molecular weight of C2-C5 hydrocarbons were especially responsible for offensive odors. Carboxylic acids based on hydrocarbons higher than C5 did not cause odors because their concentrations did not exceed the TOC values *(18)*. The strongest and the most unpleasant odor was due to butanoic acid. Its concentration was higher at 0.05 ppm in the air sample collected during 320°C extrusion. The sample taken at 280°C had 0.02 ppm. The total amounts of carboxylic acids were higher at 0.13 ppm in the air sample taken during extrusion at 320°C than in the sample taken at lower temperature with 0.06 ppm.

Some ketones with offensive smells also occurred in both air samples. Methyl isobutyl ketone (MIBK) caused an unpleasant odor. Its description was pungent in the sample taken at 280°C, and the description was sweet and pungent in the sample from 320°C. 7-octen-2-one was the reason for the unpleasant smell. It caused a dirty, plastic odor in both samples. Its amount was higher in the sample taken at 320°C. The total amount of ketones was twice as great in the air sample collected at 320°C at 0.22 ppm compared with the air sample taken during extrusion at 280°C at 0.10 ppm.




*4. Total concentrations of the carbonyl compounds in mg/m³ in air samples*

The largest peak in both collected air samples was 2,2,4,6,6- pentamethylheptane. This caused a bad, burned, plastic odor. Other hydrocarbons were present, but they did not cause any odors.

## SUMMARY

VOCs develop in the polyethylene layer during extrusion coating. We tested the cast extrusion coating samples of LDPE for liquid packaging made at two different temperatures to determine the compounds responsible for off-odors. At high temperature, a special mixture was incorporated as an additive. The compounds emitted to air during extrusion of molten resin were also identified. The purpose of this study was to determine the compounds that cause odors near the extruder, the concentrations of these compounds, and whether they exceed the exposure limits.

Using sniffing during GC/MS analysis allowed identification of the off-flavor compounds. Two methods for introducing the samples into the GC/MS were the dynamic head space method using purge and trap equipment for extrusion coating samples and the thermal desorption system for collected air samples. A semi-quantitative external standard method estimated the concentrations of smelling compounds *(19)*.

The compounds noted to cause off-flavors were carbonyl compounds such as aldehydes, ketones, and carboxylic acids. Most compounds present in extrusion coating samples and air samples made at high extrusion temperature of 320°C also occurred in samples made at low extrusion temperature of 280°C but at much lower levels. When using the additive in an extrusion coating sample for reducing off-flavor formation in LDPE processing, more dissimilarities occurred. In air samples collected during extrusion coating, the concentrations of odorous compounds did not exceed the exposure limits established for health risks. The concentrations of some compounds noticeably exceeded the values of TOC. Raising the extrusion temperature increased the amount of off-odors. Higher extrusion coating temperatures gave more off-odor causing compounds. When using a special additive in the film sample at high extrusion coating temperature, the odors decreased. TJ

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