USING GAS CHROMATOGRAPHY TO INVESTIGATE THE CAUSE OF MALODORS IN MOLDED POLYMERS:

A CASE STUDY

By

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ABSTRACT

Malodors are commonly detected in molded polymers used for general purposes such as household items, domestic appliances, plastic furniture, wheel and bumper covers in the automotive industry, and laboratory equipment. Research indicates that such strong odors are associated with the emission of harmful substances and volatile organic compounds (VOCs). Above a certain level of tolerance these volatile compounds have long-term effects detrimental to health after frequent exposure. This thesis seeks to investigate some of the compounds present in a molded polymer used by Company C in their finished product using gas chromatography and suggest ways to minimize or eliminate the smell without compromising other physical and chemical properties of the final polymer. Every stage of the production process from start to finish was analyzed, including formulation, compounding and molding. Blind odor tests were performed using the same group of panelists to determine which ingredients or molded polymers had the best or worst odor. Next, gas chromatography analysis was used to investigate what compounds were contributing to the smell detected by the panelists. Finally, several iterations of new formulations were made based on the overall analysis of the individual ingredients. The formulation that emerged best, with regards to the complete test specification, especially smell, is recommended for use in molding the new polymer.

DEDICATION

First and foremost I would like to thank almighty God for having brought me this far. I could not have accomplished any of my achievements by my might alone, and I am extremely grateful for the mercies and graciousness you have extended to me.

This thesis is also dedicated to my husband, Noah Lofquist, who has been a great support through the tough times and who motivated me to pursue my career in chemical engineering.

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CHAPTER I

INTRODUCTION

The purpose of this thesis is to investigate the cause of smell in an injection molded polypropylene polymer supplied by Company B and suggest ways to improve it. Throughout this thesis, arbitrary names have been assigned to the companies involved to maintain privacy. Company A is a raw material compounder of the raw polypropylene pellets. Company B is the supplier of the injection molded polymer, and Company C uses the molded polymer in their end product. In the manufacturing process, the raw materials and their ingredients are compounded and molded into polypropylene pellets by Company A. The pellets are then shipped to Company B and are used in making the molded polymer, which is then used by Company C in their finished product. Eliminating the source of odor and improving this molded polymer was essential to Company C because of their commitment to their customers to have zero smell in their finished product. Although most people are accustomed to the smell of the finished product of Company C, research has shown that finished molded polymers with such a strong odor emit harmful substances and volatile organic compounds (VOCs). Above a certain level of tolerance these volatile compounds have long-term effects detrimental to health after frequent exposure. Prior attempts to improve odor conditions included a suggestion by the headquarters of Company C to try formulations with low odor talc and higher melt flow, but such attempts did not improve the odor.

From previous literature, several techniques and odor analysis equipment have been employed to investigate the causes of odor, and several compounds had been determined to be contributors to odor.

In one such application where the off-odors and volatile organic compounds (VOCs) present in a food package film made from recycled polypropylene feedstock were being identified, a thermal- desorber with gas chromatography was used [1]. This technique qualitatively and quantitatively determines the levels of VOCs from this polypropylene polymer at warmer temperatures. This was necessary since the temperature at which food in these packaged containers is heated could approach temperatures at which VOCs could be emitted from this polymer. The study reported the absence of off-odors in films made under similar conditions using new polypropylene resin. However, it reported the presence of over 175 VOCs present in both films [1]. Some of the common compounds found in the study were: phthalates—which are used as plasticizers in molded plastics; mold release agents such as paraffinic hydrocarbons; butylated hydroxytoluene used as antioxidants; and phenols with phosphoric acid. The study reported odiferous substances such as N-N dimethylformamide; toluene; and 7 to 9 carbon chain aliphatic and olefinic hydrocarbons as present in the polypropylene film made from the recycled resin [1].

Similar research into a polyethylene polymer used in food applications identified odiferous volatile organic compounds which may be emitted when the polymer undergoes thermal oxidation. This study used gas chromatography with olfactometry. The study identified several of the odiferous compounds as saturated and unsaturated aldehydes and ketones with 6 to 9 carbon chains. Some of the terms used to describe the odors were: waxy, pungent, fruity and herbaceous [2].

In another application, an electronic nose array was used to determine the amount of VOCs in a carbon black polymer by exposing it to a homologous series of alcohols and alkanes [3]. The study showed that when the same concentration of alcohols and alkanes were exposed to the olfactory epithelium of the electronic nose and that of humans, there was no difference in the smell detected by the human nose and that of the electronic nose array [3].

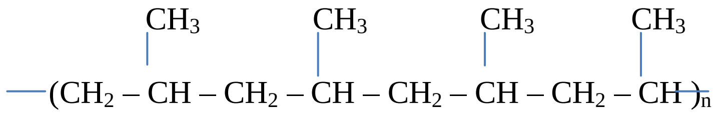
In this work we have chosen to use gas chromatography - mass spectrometer in combination with human panelists. The plan for the course of action in resolving this issue of a malodorous polymer product was to analyze every stage of the production process from start to finish. It started with the compounding process at Company A, analysis of the ingredients (resin and additives) at Company C's lab, and studying the molding process of the final product at Company B. A visit was made to Company A, and their process of making the pellets was observed. Samples of each of the ingredients - resin and additives including the low odor talc previously recommended by the headquarters of Company C - were presented for analysis. This initial evaluation was to determine if the problem was a process issue or an ingredient issue. If a process issue were identified, then investigations would commence in order to determine which process parameters needed to be adjusted in order to achieve optimum results and get the final polymer to meet Company C's standards. If a raw material issue were identified then investigations would commence to identify alternative additives that would minimize or eliminate the smell without compromising other necessary physical and chemical properties of the final polymer.

CHAPTER II

BACKGROUND INFORMATION

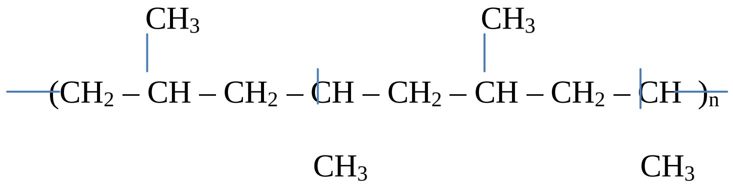
Polypropylene has numerous uses. It is used for making household goods such as toys, luggage, bottle caps, bowls, buckets, and food processor housings. It is also used in the automotive industry for parts such as battery cases, bumpers, steering wheel covers, air distribution assembly connectors, brake fluid reservoirs, and so on. Other uses of polypropylene are for coarse fiber products such as filament yarns, woven carpet backing, and fine fibers. It is also used in domestic appliances such as dishwasher parts, washing machines, refrigerator parts, and more. Further uses for PP are in food packaging, pipes and fittings, and furniture [4, 5].

Polypropylene (PP) is produced by the polymerization of the monomer units of propylene. There are three types of polypropylene formed during the polymerization process. The PP product is known as isotactic PP if the methyl groups are located on the same side of the winding spiral molecule chain. If the methylene groups are attached to the polymer backbone in an alternating manner, then the polymer is known as syndiotactic PP. An atactic PP is formed if the methyl groups are located in a random order in the polymer backbone. Of these three kinds, it is only the isotactic PP that has the necessary properties required to make a useful plastic material. Figures 1, 2 and 3 show the structure of the three types of PP formed during the polymerization process.



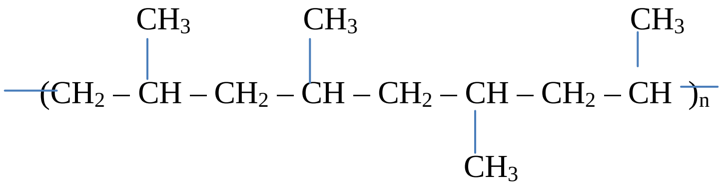
$$-(CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{CH_3}{\overset{|}{CH}})_n-$$

Figure 1 Isotactic polypropylene



$$-(CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \underset{CH_3}{\underset{|}{CH}} - CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \underset{CH_3}{\underset{|}{CH}})_n-$$

Figure 2 Syndiotactic polypropylene



$$-(CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{CH_3}{\overset{|}{CH}} - CH_2 - \underset{CH_3}{\underset{|}{CH}} - CH_2 - \overset{CH_3}{\overset{|}{CH}})_n-$$

Figure 3 Atactic polypropylene.

PP is a very high-volume commodity plastic due to its numerous uses, low cost, and properties for engineering purposes compared to other competitive thermoplastics such as polyethylene, polyvinyl chloride, polystyrene and acrylonitrile butadiene styrene (ABS) [4].

PP has lower density which makes it lightweight and useful for applications like plastic bags that require a ductile material. Furthermore it has higher stiffness and resistance to temperatures which makes it ideal for transfer of hot liquids and gases. PP has significantly higher mold shrinkage and thermal expansion with lower impact strength compared to polyvinyl chloride, acrylonitrile butadiene styrene and polyethylene. PP also provides good chemical fatigue which makes it excellent for applications that require the use of acids and bases. PP provides good environmental stress cracking, detergent resistance, and hardness. In addition, it provides the advantage of easy machining and processibility during injection molding and extrusion [4].

Some disadvantages of PP compared to the other plastics are that it has poor resistance to UV light and gamma radiations. It also has poor oxidative resistance, difficult solvent and adhesive bonding, and suffers from high creep under sustained load [4]. Most of these disadvantages however, can be partially or completely overcome by selecting materials appropriately, incorporating additives, and/or using specific processing techniques.

PP by itself is not hazardous to health, but it can release volatile organic compounds (VOCs) into the environment at high temperatures which could be occasionally reached in some of Company C’s applications.

The Polypropylene Compounding Process at Company A

In the process of making the polypropylene pellets at Company A, all the powdered and solid ingredients are mixed together in a tank. They are then fed into the barrel of the extruder, where the desired melt temperature of the molten plastic is achieved. There is regulation of the temperature to lower the risk of overheating, which may cause degradation in the polymer. From the extruder, the molten polymer goes into a screen plate where impurities are removed. This screen plate also generates a back pressure which drives and converts the molten plastic into the linear longitudinal polymers. These are then cooled in a set of cooling rolls and enter the die. Afterwards, they are then cut into the polypropylene pellets using an underwater die face cutter.

At Company A, the primary ingredients used in their process are: resin, talc, color, lubricant, distearyl thio dipropionate, epoxy, and a stripping agent. The main ingredient used in the compounding of the final pellet for molding is the polypropylene resin. All the other ingredients are additives or mineral fillers.

Investigation into the Significance of Each Ingredient in the Compounding Process

Resin

This is the polypropylene resin and forms the base for the production of the polypropylene pellets. Although the resin did not have a bad odor at the temperature of the smell test, some resins, at a much higher temperature - such as in the extrusion or molding process - can emit substances which can cause odor. Hence an investigation was conducted into the types of resin and their properties. This was to see if the type used in our application was capable of producing odor.

In choosing the best grade of polypropylene resin, four factors of importance are considered:

1. Type – either a homopolymer or a copolymer
2. Polymerization technique: reactor or rheology grade
3. The defined melt flow rate required
4. Appropriate additive system

There are two major types of polypropylene resin – homopolymers and copolymers. The other types fall under one of these major categories.

Homopolymers by definition are “polymers derived from one species of monomer.” The polymerization process in homopolymers is done in the presence of a stereospecific catalyst [6]. This makes them more rigid and gives them better resistance to higher temperatures than copolymers. Thus at room temperature homopolymers are slightly stiffer than copolymers. On the other hand, their impact strength at temperatures below zero degrees Celsius is limited. Examples of practical applications where this type of polymer is used are hair dryers, irons, and car mounting components.

Copolymers are homopolymers copolymerized with ethylene. Although they give a softer feel to their corresponding film and fiber products, they are more expensive than the homopolymers. There are two types: random copolymer and block copolymer. The block copolymers have much higher ethylene content than the random copolymers. This makes them much tougher so that they can withstand higher impact even at low temperatures [4, 7].

The Polymerization Technique

The polymerization technique determines the molecular weight of the polymer. There are two major techniques used in the polymerization of the polypropylene resin. The technique leads to either a reactor grade or a controlled rheology (CR) grade resin.

The controlled rheology grade technique can be used both on homopolymers and copolymers. It involves splitting the PP chain into smaller units in the post-reaction stage. This decreases the molecular weight to a range of approximately 3 to 5 units, which subsequently leads to an increased melt flow rate. One advantage of using this technique with low molecular weight is that it reduces shrinkage and warpage. Another advantage is that the injection pressure is lowered due to the easy flow of the material [4].

A major disadvantage to this technique is that low molecular weight polymers or oligomers could be formed due to the breakdown of the polymeric chains, and these can cause odor problems also known as organoleptic problems in polypropylene. Oligomers are polymers with fewer monomer units. Another disadvantage due to the low molecular weight is the decrease in impact strength of the polymer [4].

Reactor grades of polypropylene have broad molecular weight distribution [4].

The Defined Melt Flow Rate

This is used to measure the viscosity of polypropylene. Hence by definition, melt flow rate is the “weight of the polymer that can be extruded through an orifice in a given time at a specified pressure and temperature” [4]. Measurement of the viscosity can be used to estimate the molecular weight of PP. The molecular weight in turn reflects the differences in length of the molecular chain. As aforementioned, high or low molecular weights have some advantages and disadvantages and eventually determine some of the mechanical properties of the final polymer.

There are basically two kinds of melt flow rate: low melt flow and high melt flow. Low melt flow rate implies slow flow and higher molecular weight but tougher and higher impact strength. This is ideal for applications that require extrusion and blow molding. High melt flow rate implies easy flow and lower viscosity and thus lower molecular weight, less toughness, and lower impact strength. This type of flow rate is ideal for applications that require the use of injection molding processes.

Company C’s standards require that the final molded polymer should not show any signs of decomposition at elevated temperatures of 150^0C after aging for about 400 hours; no fracture or cracking during a ball drop test; high flexural modulus; and melting temperature greater than 152^0C. Based on these requirements and the properties discussed above, we expect our polypropylene resin to be a high melt flow rate homopolymer. Should the choice of resin above be true of the PP resin, then we expect low molecular weight oligomers being formed at high temperature which can cause odor issues.

Appropriate Additive System

Additives are substances added to the polypropylene resin to improve its properties. This is because the raw PP resin is very unstable and easily susceptible to air oxidation and deterioration within a short period of time. Hence the addition of additives helps stabilize the PP and make it a more versatile plastic. The type of additive added determines what functionality in the polymer is improved. However, one essential thing to note is that in general, improvement in a particular property due to the addition of an additive(s) can be at the expense of another useful property. One disadvantage is that during processing some of these additives can produce toxic degradation products. The additives used in the final PP pellets are: talc, color, epoxy, DSTDP, lubricant and a stripping agent [3, 5, 7].

Talc

Talc is used as mineral reinforcing filler in the final PP pellet. This inorganic filler can be used both in homopolymer and copolymer grades of PP. The percentage by weight normally used ranges from about 10 to 40%. The amount of filler used determines the properties of the filled grade polypropylene. One advantage that this type of filler provides is that not only does it lower the amount of resin to be used and thus reduce cost, it also enhances the performance of the final polymer. Some improved properties include enhanced heat deflection temperature, reduced mold shrinkage, and improved scratch and mar resistance. The heat deflection temperature measures the performance of the final PP under load at elevated temperatures. Talc also acts as an antiblocking agent. It prevents the polymer film or product from sticking to itself.

The purity and particle size distribution are just two of the important things needed to achieve consistent quality talc – filled PP product. It is therefore important to use a good grade of talc with lower iron content. If lower iron content is not used, there will be high metallic impurities which may result in the lack of stability of the final formulation [4, 5, 7, 13].

Epoxy

Epoxy is used as a talc deactivator. Its function is to coat the talc. Purity and particle size distribution of the talc are some of the important things needed to achieve a consistent quality talc filled PP product. Metallic impurities in talc can alter the stability of the final formulation. Talc contains iron-based impurities which catalyze the decomposition of hydroperoxides. One of the ways to avoid talc decreasing the stability of a stable resin is by the addition of epoxy. Epoxy prevents the decomposition of hydroperoxides by forming a complex with the iron in the talc [5, 7, 13]

Color

Color is used as a pigment to improve the appearance of the final molded polymer and to render it opaque. This is necessary because the raw resin is translucent. Color also has some impact on the stability and physical properties of the final product. The major effects are thermal stability and UV light stability [5, 13].

Lubricant

Lubricant is used as an antistatic agent. The main active ingredient present and most commonly used lubricant for our application is glyceryl monostearate – a nonionic antistatic agent. Polypropylene has high electric resistance and therefore tends to accumulate an electrostatic charge. Not only does this disadvantage cause dust to form in an unattractive pattern on articles made from it, it also presents a hazard for the possibility of sparks in applications where explosive fumes may be present [4,5,13].

Lubricant, however, has little or no effect on the chemical, mechanical, and thermal properties of the PP. Usually, only a small percentage of about 1% by weight is required to perform its function. For our application, the lubricant is not a necessary ingredient and can be removed from the compounding ingredients if it will improve the odor problem [5,7,13].

DSTDP

Distearyl thio dipropionate (DSTDP) belongs to a group of compounds used as secondary stabilizers. Its function is for long-term heat aging (LTHA). Secondary stabilizers do not have any appreciable value when used in the resins by themselves, but work synergistically in combination with a primary stabilizer. For example, at oven temperatures of 150^0C, thioesters such as DSTDP yield no appreciable long-term heat aging. Hindered phenol - a primary stabilizer - by itself gives the polymer a lifetime of 20 to 35 days at the same temperature. But when combined, the two stabilizers could yield a lifetime aging of 80 to 100 days [5].

Stripping Agent

Stripping agents are used to reduce odor and VOC emissions in the compounding process. They are easy to use and have no negative influence on the mechanical and optical properties of the final PP pellet. It is, however, recommended to evacuate with a vacuum of minimum 100 mbar for highly effective removal of odor and VOC emissions. Furthermore, it is essential to have a degassing vent shortly in front of the end of the extruder [9, 10].

CHAPTER III

METHODOLOGY

Smell Test

Because odor is highly subjective, measuring odor is challenging. Company C uses a traditional smell test during which human panelists evaluate odor on a scale from 1 (no perceptible odor) to 6 (unbearable odor). In performing a smell test, a small amount of the polymer to be investigated is put into a scrupulously clean jar and heated to the specified temperature between 70°C and 90°C for the specified amount of time. The jar and its contents are then allowed to cool for about 5 minutes. The panelists then smell the released volatiles by cracking the lid of the jar. A smell rating of 3.5 and below is considered a pass while a rating higher than 3.5 is considered a failure.

Detailed Analysis into the Problem Additives

Each additive that failed the initial smell test was analyzed in order to gain scientific insight into why these additives failed the smell test. An in-depth analysis of each failed component was performed using GC/MS with pyrolyzer. This was to investigate what compounds (volatiles, additives, impurities) present in these additives could be contributing to the bad smell.

EGA Analysis

The first experiment performed was an Evolved Gas Analysis (EGA). The International Confederation for Thermal Analysis (ICTA) defines EGA as “a technique to determine types and/or quantities of volatile components evolved from a material as a function of temperature by varying the material temperature according to a controlled program” [11]. The equipment used in performing this analysis was the multi – shot pyrolyzer (EGA/PY-3030D, Frontier lab, Japan), an auto-shot sampler (AS-1020E, Frontier Lab) and a gas chromatograph (GC 7890A, Agilent Technologies, California) with mass spectrometer (MSD 5975C, Agilent Technologies, California).

In EGA analysis, each sample of about 1 to 3 mg is weighed into an eco-cup and placed into the auto sampler. The normal ultra-alloy capillary column (UA5 -30m X 250µm X 0.25µm, J&W, Wantanabe) in the GC/MS is replaced with an EGA transfer line (capillary tube). Next, the furnace temperature is programmed from a lower temperature of about 100^0C and ramped up to a high temperature of about 800^0C at a rate of 10^0C per minute. The sample is dropped from the auto sampler to the double shot pyrolyzer as the experiment proceeds. Vapors evolve as the sample is heated. The vapors are swept through the split/splitless injection port where a fraction of the gases pass through the EGA capillary tube (UAD TM -2.5N, Frontier Laboratories Ltd.) which is kept at 300^0C to prevent condensation. The gases are detected by a mass spectrometer based on their ion masses. A plot of the sample temperature against the detector response is called a ‘thermogram’. Here the individual peaks are then analyzed based on the retention time and transition from one peak to another. Further analysis of the individual peaks is performed using double shot analysis [11].

Double Shot Analysis

Double shot analysis involves further analysis of the individual peaks. Double shot analysis has two parts to it. The first part of the analysis is called the thermal desorption portion where volatiles, additives, impurities, residual solvents, etc. are detected. The temperature range of analysis is usually ramped up from 100^0C to about 300^0C**.** Since each polymer and ingredient has its own unique characteristics, a second thermal desorption method can be set up to further analyze each polymer if needed. This is based on the temperature profiles from the thermogram in EGA analysis [11]**.**

The second part of the double shot analysis is pyrolysis where there is complete degradation of the polymer. The identity of each compound is determined by doing a library search of the chromatogram against the finger print or spectrum of the candidate compounds. A quality match and visual inspection of the spectra against the compound in the library is used to identify which compound or polymer might be present. Further qualitative analysis of the prospective compounds is performed using the Q-editor function in the equipment's software. The Q-editor is a function in the chemstation (E.02.02.1431, copyright 1989-2011, Agilent Technologies Inc.) data analysis software that is used to quantitate and calculate the percentage composition of compounds determined by gas chromatography.

In performing the double shot analysis the transfer line is removed and replaced with a UA5 column. Again, scans are made to detect any leaks and about 1 to 3 mg of each sample is weighed into an eco-cup and placed into the auto sampler. A cryogenic trap which uses liquid nitrogen for cooling is also set up. Next, a sequence is set up in both the chemstation software and the frontier pyrolyzer software. Each "method", which has already been created for each sample based on the temperature profiles from the EGA, is loaded. The data of chromatograms from each set up is then analyzed.

A different method using the range of 100^0C to 300^0C for general thermal desorption analysis was used for all the additives. This was to investigate if additional or different compounds would be emitted. In each case, however, similar compounds were emitted. This confirmed that the previous compounds found were actually present.

Subsequently, each of the main ingredients that failed the odor test was analyzed. An EGA analysis was performed on each of its additives. Next, a double shot analysis was performed based on the thermogram from the EGA analysis.

Analysis of the Chromatograms Using NIST and F-search

In analyzing our chromatograms, two different library searches were used. These are the National Institute of Standards and Technology (NIST) library (Copyright 2011) and the F-Search library (Version 3.10. copyright 2009, Frontier Laboratories Ltd).

Analysis Using NIST Search

Procedures 1 to 8 in appendix B outline the steps used in analyzing the chromatograms and determining what compounds were actually being emitted from each additive using the NIST library, with color as an example.

Figures B.1 and B.2 in Appendix B show results of the EGA thermogram and double shot chromatograms for color respectively.

From the analysis, the compounds found using the NIST library search were: 6-methyl-3, 4-dihydro-2-H pyran, octamethyl-cyclotetrasiloxane, 2, 4-dimetyl-1-heptene, octamethyl cyclotrisiloxane, 1-octadecene, 5-octadecene, eicosane, octadecanoic acid, and pyrene.

F- Search

This library contains 268 polymers, including newly developed or specially modified polymers that are commercially available, and 358 additives that are widely used in industry. Since this search focused on identifying volatiles, additives, solvents, residuals, and impurities, the additives library (ADD –MS08B.fl) with its data source from the thermal desorption GC/MS libraries was used.

The compound search was performed using similar steps from procedures 1 to 6 as in the NIST search above. The list of compounds found to be present in the F-search library were: 2, 4-dimethyl-1-heptene, 1-nonadecene, stearic acid, and distearyl-3, 3-thiodipropionate. Table B.2 in Appendix B gives the list of compounds found to be present in both the NIST and F-search libraries.

Analysis of Blank Samples

To avoid contamination of samples from one cup to another, empty cups were positioned for run between each sample. Analysis of the blank indicates there was no sample contamination from the previous cup to the next. However, siloxanes and cyclotrisiloxane were consistently found at retention time (RT) of 3.334 and 4.911. Knowledge of the type of column being used indicates the possibility of a column bleed. In addition, siloxanes could come from equipment sources such as the septum. The presence of ions 73 and 207 m/z in the total ion chromatogram (TIC) was a clear indication of a septum bleed [12]. Hence, siloxanes and its constituents - although the compounds had good peaks - were not included in the list of compounds emitting out of our additives.

Figure C.1 in Appendix C shows the mass spectra of the siloxanes found in the blank at a similar retention time.

CHAPTER IV

RESULTS

Results and Analysis of Individual Ingredients

All the ingredients used in Company A’s formulation including the low odor talc, were requested and individually tested for smell using Company C’s standards. To ensure the reliability of the ratings, the blind smell test was conducted three times using random sampling.

Table A.1 in appendix A summarizes the results of the overall smell rating of the individual ingredients by eight panelists and their comments. A smell rating of 6 indicates the worst smell and a rating of 1 indicates the best. A rating of 3.5 is considered unacceptable by Company C. Figure 4 gives the graphical representation of the results.

This preliminary investigation revealed that the primary ingredients that may contribute to the smell are: color additive, the heating agent (DSTDP), and possibly the lubricant. This is because these three ingredients failed the smell test. It is not surprising that the smell rating of the final product - polypropylene pellets - also failed the smell test.

The old resin actually had a better smell rating than the new resin. This could explain why previous attempts to try formulations with high melt flow rate did not improve odor condition. This is because despite the difference in grade, high melt flow rate constitutes a low molecular weight polymer and thus the issue of odor problems at high temperatures will still persist. Inquiries into the resin type and grade from Company A indicate that the current resin is

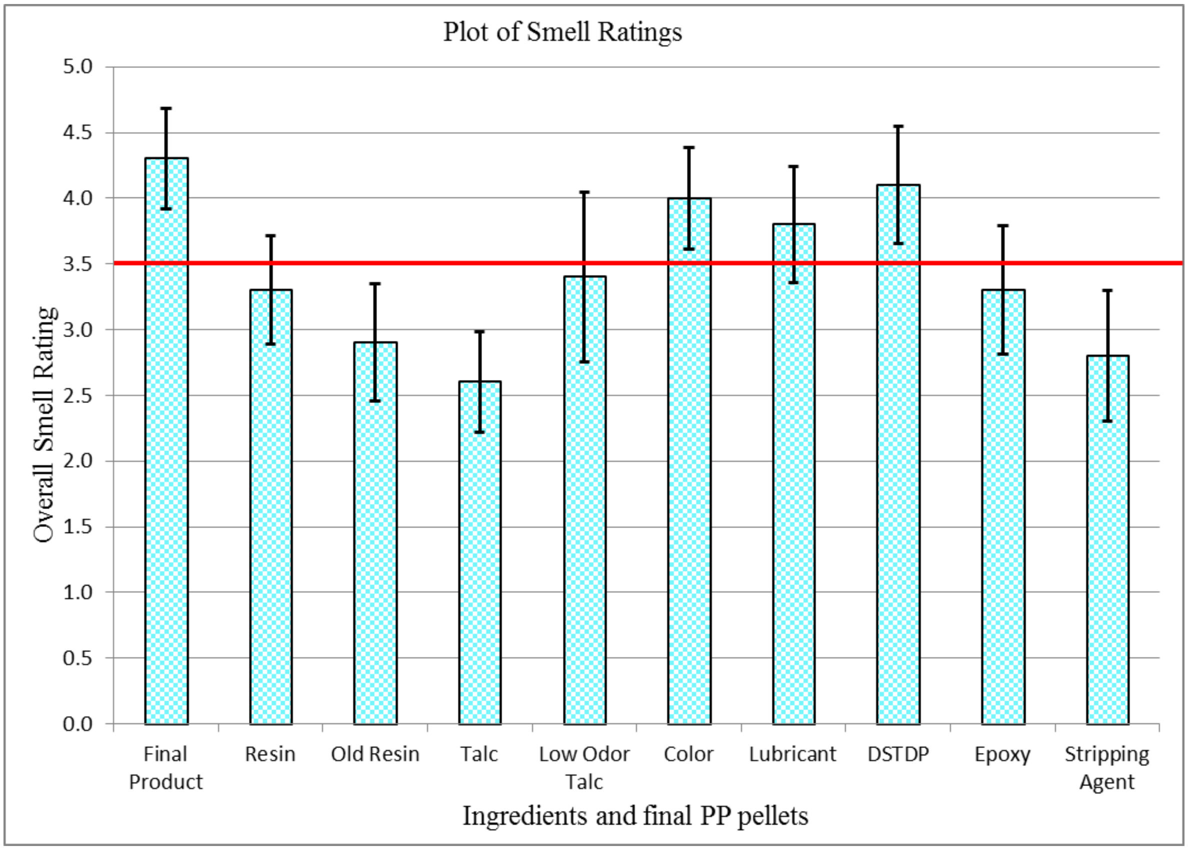


Figure 4 Plot of smell rating against the individual ingredients and the final PP pellets.

actually a reactor grade, medium melt flow rate homopolymer. Had it been a controlled rheology grade, worse smell would be expected.

Since for the application a high melt flow rate homopolymer will be the wisest choice, further investigation was conducted into the various trade name resins and what improved process parameters are set in place to remove volatiles and odor after the resin is produced. The research indicated that the Novolen resin could be a better alternative over the other major polypropylene manufacturers.

In the Novolen process, the reactants – ethylene, propylene and other desired comononers are fed into the reactor and the polymerization conditions and parameters are set based on the grade of polymer being made. The resulting mixture is then fed into the reactor and the polymer powder is discharged from the reactor and separated from the unreacted monomer which is recycled into the reactors. The polymer is then flushed into a nitrogen purge vessel (degasser) to strip it of residual propylene. The powder is then converted into pellets after addition of the required additives in an extruder. This process offers an optional degassing unit to treat the pellets after extrusion for applications that require extremely low volatiles and odor levels [8].

Since the manufacturer of the resin is proprietary to Company A and cannot be disclosed, the possibility of switching resins was not an option. Hence no further action and investigation was conducted. Instead, we worked within the parameters that could effect a change. Thus, the additives became the focus of investigation. It is suggested, however, that in future applications, Company A looks into other resin manufacturers to see if a change in resin could produce a better outcome.

The three ingredients that failed the smell test were individually analyzed to determine the specific components that could be contributing to odor.

Original Color Additive

Table 1 gives the compiled list of compounds found to be present in the color additive using both the NIST and F-search libraries. A look at the list indicates the presence of compounds such as octadecanoic acid. Octadecanoic acid belongs to the functional group of compounds known as carboxylic acids. Low molecular weight carboxylic acids can undergo oxidation which can result in malodors. Another compound of concern is distearyl-3, 3-thiodipropionate (DSTDP). Thiols are sulphur containing compounds and have a very bad odor to them. The presence of a sulphur containing compound could explain why this color additive

Table 1   List of compounds from both NIST and F-search libraries

Table 1	GC/MS COMPILED RESULTS FROM LIBRARY SEARCH FOR COLOR		
Peak No.	Retention Time (mins)	Library/ID	Quality Match
1	3.042	2-H Pyran, 3,4 - dihydro - 6 - methyl-	91%
2	3.544	2,4 - Dimethyl - 1- heptene	90%
3	11.929	1- Octadecene	99%
5	12.011	5 - Octadecen, (E) -	94%
6	12.881	Eicosane	89%
7	13.056	Octadecanoic acid	90%
8	14.329	Octadecanoic acid	99%
9	14.370	Pyrene	95%
10	22.066	Distearyl-3,3'-thiodipropionate	85%

had such an offensive smell. Hence a different color additive was suggested as a substitute by Company A. The original color additive was furnace black which was used for general purposes. The new color package is chanel black which is of higher purity than the old one.

New Color Additive (P7D)

This color additive is known as P7D. Unlike the previous color additive, this additive is FDA approved and is usually safe to use even for food applications. It does have the same properties as the old one and will serve the same function without emitting all the volatiles. In addition, due to the position and use of the final molded polymer in Company C’s finished product, color matching was not a necessary requirement. Consequently, the new color additive could be substituted without any adverse effects on the final product.

A blind smell test of the new color additive was performed together with the old one. The results of the smell test shows an average smell rating of 4.2 for the original color additive and an average rating of 3.3 for the new color additive. Hence, the new color additive was significantly better than the old one. Table 2 and figure 5 shows the results of the smell ratings by the same panelists as before.

Next, the GC/MS with pyrolyzer was used to analyze the compounds emitting from the new color additive. Figures B.2 to B.10 in Appendix B show how the final lists of compounds present in the new color additive were determined.

Analysis of this additive indicates that the only compound possibly emitting from the new color additive is carbonic acid, octadecyl 2, 2, 2 – tri chloroethyl ester. Since we were not certain of its spectra, it would be safe to say that barely any compounds are being emitted from the new color additive.

Comparison of the two different color additives gives clear scientific evidence why one compound would have a worse odor than the other. Figure C.6 in Appendix C compares both color additives side by side.

Heating Agent (DSTDP)

In analyzing the remaining problem additives, the same techniques, steps, and procedures as outlined above for color were used. First, an EGA analysis was performed followed by a double shot analysis. Figures D.1, D.2 and Table D.1 in Appendix D show the results of the EGA thermogram, double shot chromatograms for DSTDP and the list of compounds found to be present in the NIST and F-search libraries respectively.

The complete list of compounds found to present in DSTDP is given in Table 3.

Table 2 Comparing the smell rating of the original color additive with the new color additive

COMPANY C

Table 2	ODOR (SMELL) TEST					
	Vase No.	Additives	Participant	Participant Rating	Comments	Average
1	SAMPLE A	Original color additive	1	4.0		4.3
			2	4.5		
			3	4.5	Aromatic smell	
			4	4.0		
			5	4.5		
2	SAMPLE B	New Color Package (P7D)	1	3.5		3.2
			2	3.0		
			3	3.5		
			4	2.5		
			5	3.5		
3	SAMPLE C	New Color Package (P7D)	1	4.0		3.4
			2	3.0		
			3	3.0		
			4	3.5		
			5	3.5		
4	SAMPLE D	Original color additive	1	4.5		4.0
			2	4.0		
			3	4.0	Aromatic	
			4	4.0		
			5	3.5		

Rating Scale :		Comment/Conclusion
Grade	Evaluation	The above color additives were submitted for a blind smell test according to standards. It can be seen that samples B and C (new color package) had a better smell rating than samples A and D
1	Not Perceptible	
2	Perceptible, not offensive	
3	Clearly perceptible, but not yet offensive	
4	Offensive	
5	Strongly Offensive	Standard: odor ≤ 3.5
6	Unbearable	

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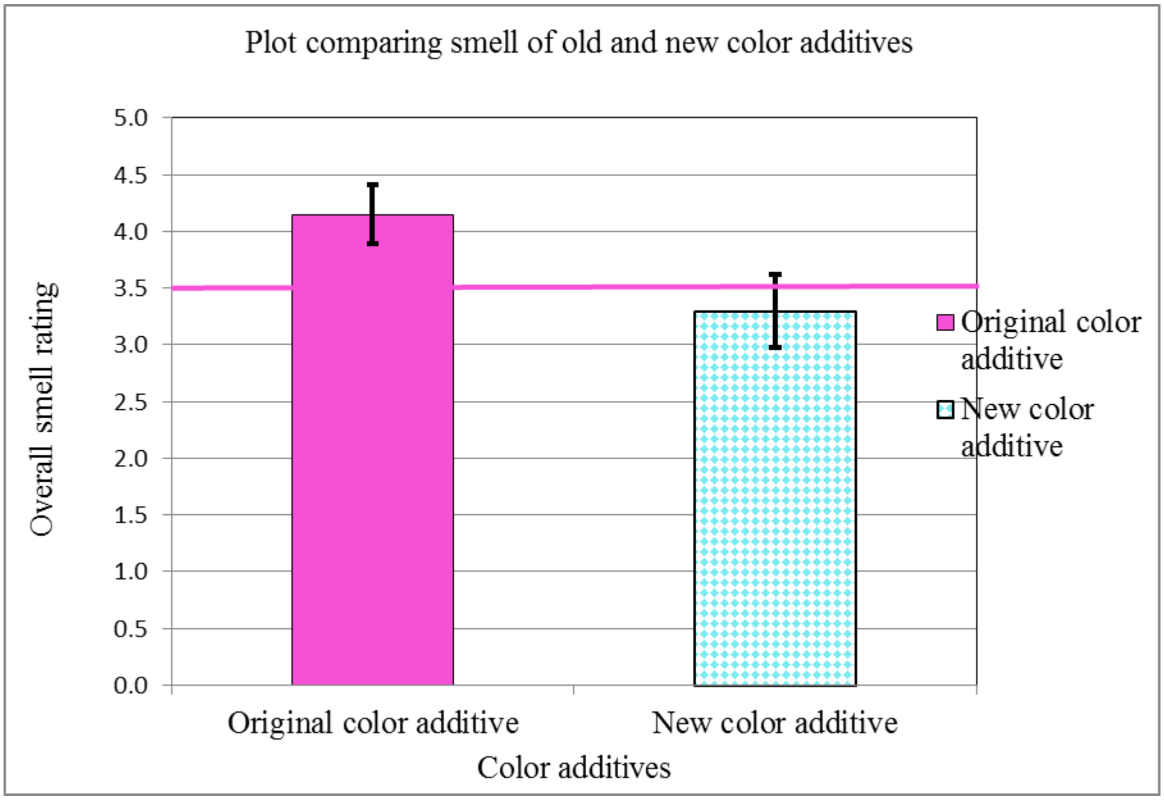

Figure 5 Graph comparing the smell rating of old and new color additives.

Table 3 Compiled list of compounds present in DSTDP

Table 3	COMPILED LIST OF COMPOUNDS FOR DSTDP		
Peak No.	Retention Time (mins)	Library/ID	Quality Match
1	14.224	1-Octadecene	99%
2	14.341	1- Heneicosene	95%
3	14.668	Phenol, 4,4 ' -(1-methylethlyidene) bis	98%
4	16.974	Octadecyl 3 -mercaptopropionate	95%
5	15.152	Acrylic acid tetradecyl ester	99%

Analysis of the Compounds

From Table 3, investigations into the characteristics of these compounds show that:

- Phenols in general have sweet and aromatic smell: With the presence of bis-phenol in this additive, one can say that this additive is capable of having an aromatic smell to it.
- Esters are sweet smelling compounds: Presence of acrylic acid tetradecyl ester indicates that one is capable of smelling something sweet from this additive.
- Carboxylic acids: Low molecular weight carboxylic acids can undergo oxidation which can result in the compound being odiferous. Presence of octadecanoic acid explains why one can perceive the smell of vinegar.
- 3-mercaptoproprionate compounds: These compounds have a horrible smell to them. The presence of 3-mercaptoproprionate octadecyl in this additive will explain why a participant will rate this as very offensive.

The main function of DSTDP is its use as a secondary stabilizer for long-term heat aging (LTHA). But it works only in combination with a primary stabilizer. However, primary stabilizers can impart a relatively good degree of stability ranging from 20 to 35 days of heat aging at 150^{0}C without the addition of the secondary stabilizer. The former only helps exhibit a higher degree of melt stability. For Company C's application the required lifetime is 400 hours (~17days) at 150^{0}C. Since we already have a primary stabilizer (butylated hydroxytoluene) present, the removal of the DSTDP will not affect the final properties of our polymer.

It is interesting to note that the smell test was conducted prior to running these samples in the GC/MS with pyrolyzer. However, from Table A.1, comments of the panelists who participated in the odor test show that they had already detected these offensive odors. Such comments were: rancid smell, vinegar, phenol, aromatic solvent.

Clearly, this additive has a mixture of some of the worst smelling substances, and therefore it was prudent to eliminate it from the compounding ingredients.

Epoxy

It became necessary to analyze this additive although it did not fail the smell test. This was to identify the compounds emitting from it and to determine if large quantities of those compounds would lead to an offensive odor.

Figures D.3, D.4 and Table D.2 in Appendix D show the results of the EGA thermogram, double shot chromatograms for epoxy and the list of compounds found to be present in the NIST and F-search libraries respectively. The compiled list of compounds possibly present in epoxy is given in Table 4.

Table 4 Compiled list of compounds present in epoxy

Table 4	GC/ MS COMPILED RESULTS FROM LIBRARY SEARCH FOR EPOXY		
Peak No.	Retention Time (mins)	Library/ID	Quality Match
1	14.831	Phosphine oxide, butyldipheyl-	78%
2	17.838	2,2 (1-methylethyl diene) bis (4,1, phenyenoxymethylene) bis oxirane	93%

From Table 4, it can be said that the main compounds present are 2, 2’-[(1-methylethyldiene) bis (4, 1, phenyleneoxymethylene)] bis-oxirane and phosphine oxide. Investigation into these compounds shows that they do not cause odor. Since epoxy is a talc deactivator and the talc content had been increased to make up for the increase in resin, a possible increase in epoxy will be necessitated. This will help prevent the decomposition of hydroperoxides by forming a complex with the iron in the talc.

Lubricant

The active ingredient in lubricant is glyceryl monostearate. Since this is a constituent of fatty acids, it has the capability of undergoing oxidation when heat is applied. The result could be a substance that has a rancid smell. Analysis was still needed to determine other compounds that might be present. Figures D.5, D.6 and Table D.3 in Appendix D show the results of the EGA thermogram, double shot chromatograms for lubricant and the list of compounds found to be present in the NIST and F-search libraries respectively.

The list of compounds possibly present in the lubricant is given in Table 5.

From Table 5, the presence of these compounds indicates that one should perceive bad odor, since carboxylic acids (palmitic acid, stearic acid) under oxidation can cause a rancid or bad smell. The presence of these ingredients is indicative of a high possibility of the final molded polymer having an offensive smell.

An analysis of the resin indicates that it has a small amount of lubricant inherited into the formulation. The additional lubricant added assists with the polymer release during the molding process but is really not required. For the application, we couldn’t anticipate any issues in the molding process if the lubricant were removed. As previously mentioned, since the lubricant

Table 5 Compiled list of compounds possibly present in lubricant

Table 5	GC/MS COMPILED RESULTS FROM LIBRARY SEARCH FOR LUBRICANT		
Peak No.	Retention Time (mins)	Library/ID	Quality Match
1	5.955	Glycerin	93%
2	13.097	n-Hexadecanoic acid / Palmitic acid	99%
3	14.41	Octadecanoic acid / stearic acid	99%
4	17.593	Stearic acid monoglyceride	97%
5	17.715	Stearic acid monoglyceride	92%

does not have significant effect on the final properties of the molded polymer, hence the decision to take it out of the formulation if need be.

Developing the New Formulations

With the knowledge of the problem additives and their raw materials, Company A compounded six different formulations for PP pellets. Next, the pellets were molded into plaques to determine if the molding process would affect the outcome of the final polymer. Of these six, only three formulations were chosen for further analysis both in pellets and plaque. This was because the other 3 pellets still failed a simple smell test at Company A. Plaques are rectangular molded polymers molded from the pellets by Company A using a lab size injection molder. The three formulations that passed the smell test at company A were:

1. Formulation 1 - Base formulation – This has all the ingredients but with the DSTDP taken out.

2. Formulation 2 – Has the base formulation but with the old color additive substituted with the new color additive (P7D).
3. Formulation 3 – Has the base formulation with new color additive and no lubricant added.

These were assigned lot numbers for easy identification and shipped to Company C for further analysis. They were:

1. Formulation 1 – S119364
2. Formulation 2 – S120167
3. Formulation 3 – S120168

Results and Analysis of the New Formulations at Company C

With receipt of the new formulations, a blind test for smell was conducted at Company C for both pellets and plaques. Table 6 shows the results of the smell test for the pellets. Table 7 shows the results of the blind smell test for the plaques. Figure 6 shows a graph comparing the smell ratings of the three new formulations in pellets and plaque.

From Tables 6 and 7 it can be seen that the smell ratings of formulations 2 and 3 emerged with good results. But overall, formulation 2 was the best, passing both in pellets and plaque. This was contrary to what was to be expected. It was expected that formulation 3 turn out the best since it had the least amount of the individual additives that failed the preliminary smell test. Finally, the three formulations were analyzed using the GC/MS and the results were compared.

Figures E.1 and E.2 in Appendix E show chromatograms, comparing the three new formulations in pellets. There were some common peaks although some have a higher peak area compared to others. Higher peak areas reflect a higher concentration of the compound.

Table 6 Smell rating of the three newly formulated polypropylene pellets

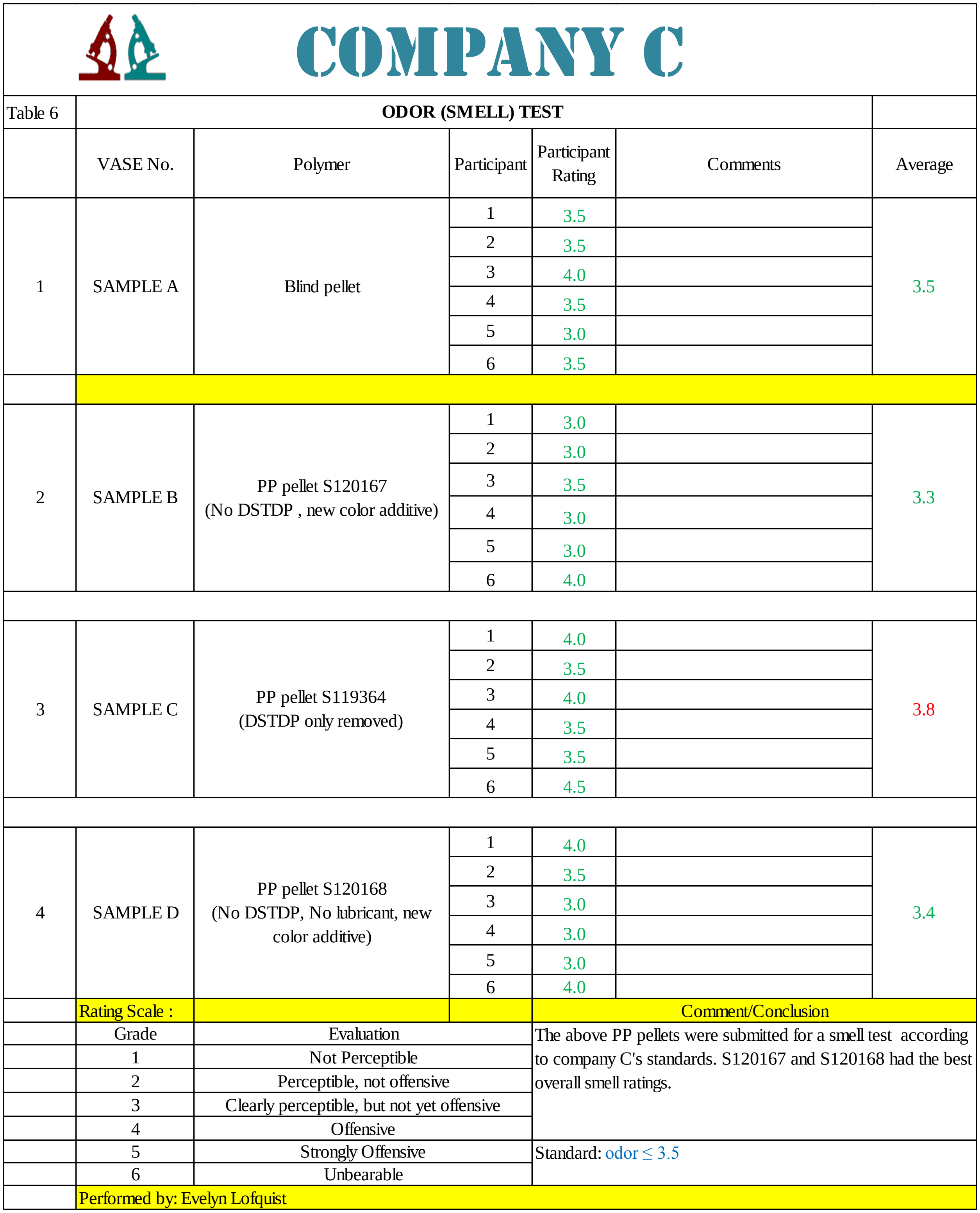

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Table 6	ODOR (SMELL) TEST					
	VASE No.	Polymer	Participant	Participant Rating	Comments	Average
1	SAMPLE A	Blind pellet	1	3.5		3.5
			2	3.5		
			3	4.0		
			4	3.5		
			5	3.0		
			6	3.5		
2	SAMPLE B	PP pellet S120167 (No DSTDP , new color additive)	1	3.0		3.3
			2	3.0		
			3	3.5		
			4	3.0		
			5	3.0		
			6	4.0		
3	SAMPLE C	PP pellet S119364 (DSTDP only removed)	1	4.0		3.8
			2	3.5		
			3	4.0		
			4	3.5		
			5	3.5		
			6	4.5		
4	SAMPLE D	PP pellet S120168 (No DSTDP, No lubricant, new color additive)	1	4.0		3.4
			2	3.5		
			3	3.0		
			4	3.0		
			5	3.0		
			6	4.0		

Rating Scale :		Comment/Conclusion
Grade	Evaluation	The above PP pellets were submitted for a smell test according to company C's standards. S120167 and S120168 had the best overall smell ratings.
1	Not Perceptible	
2	Perceptible, not offensive	
3	Clearly perceptible, but not yet offensive	
4	Offensive	
5	Strongly Offensive	Standard: odor ≤ 3.5
6	Unbearable	

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Table 7 Smell rating of the three new formulations in molded plaques

COMPANY C

Table 7	ODOR (SMELL) TEST					
	VASE No.	Polymer	Participant	Participant Rating	Comments	Average
1	SAMPLE E	Molded Plaque S119364 (DSTDP only removed)	1	3	Blind Molded Polymer	3.7
			2	4.5		
			3	4.0		
			4	3.0		
			5	3.5		
			6	4.0		
2	SAMPLE F	Molded Plaque S120168 (No DSTDP , new color additive)	1	3.0		3.5
			2	3.0		
			3	4.0		
			4	3.5		
			5	3.0		
			6	4.5		
3	SAMPLE G	Blind Molded Polymer	1	3.0		3.5
			2	3.5		
			3	3.5		
			4	3.0		
			5	3.5		
			6	4.5		
4	SAMPLE G	Molded Plaque S120167 (No DSTDP, No lubricant, new color additive)	1	3.0		3.2
			2	3.0		
			3	3.0		
			4	3.0		
			5	3.0		
			6	4.0		
	Rating Scale :			Comment/Conclusion		
	Grade	Evaluation		The above Plaques were submitted for a smell test according to standards. Reults show that S120167 and S120168 had the best overall smell ratings.		
	1	Not Perceptible				
	2	Perceptible, not offensive				
	3	Clearly perceptible, but not yet offensive				
	4	Offensive				
	5	Strongly Offensive		Standard: odor ≤ 3.5		
	6	Unbearable				
	Performed by: Evelyn Lofquist					

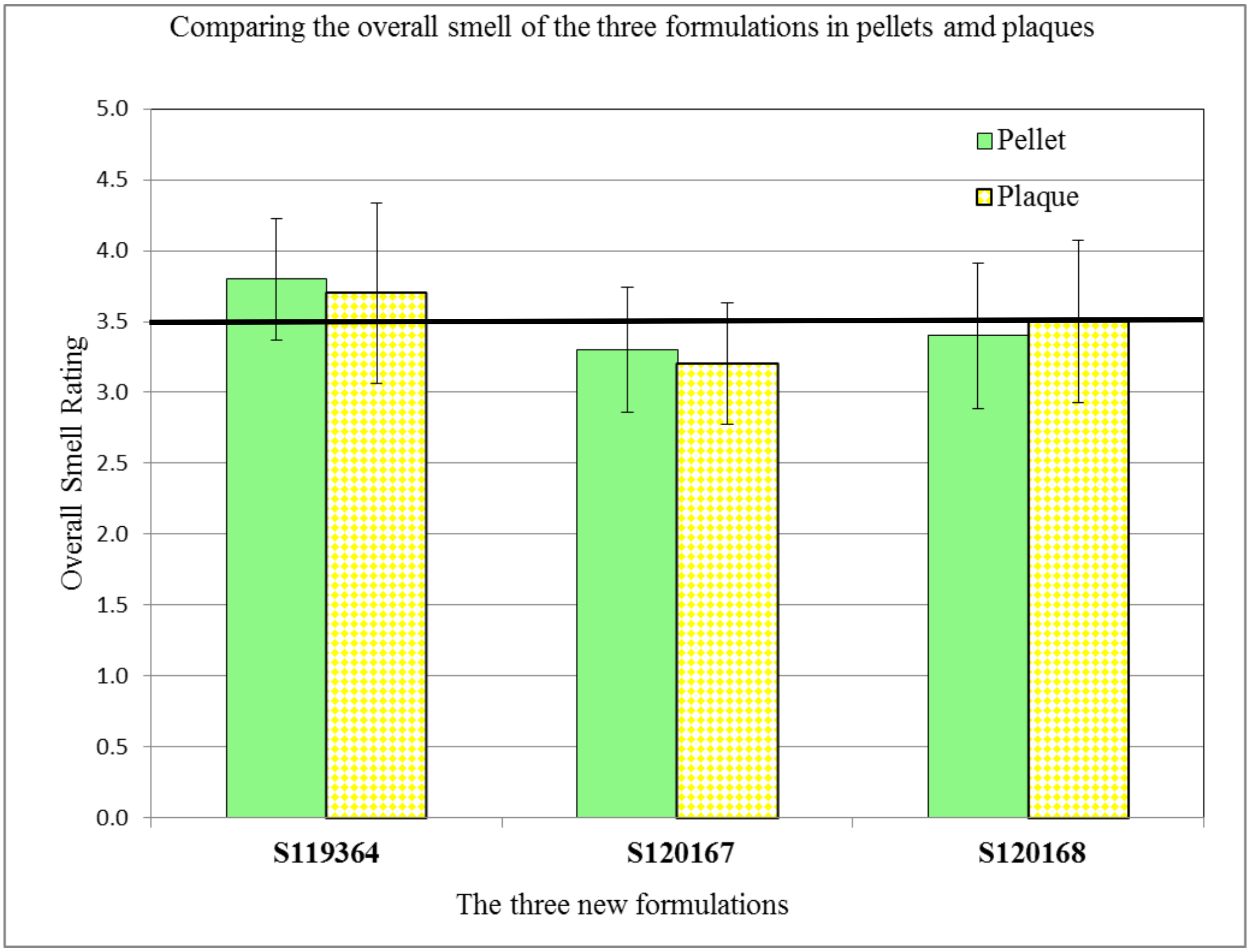

Figure 6 Plot comparing the overall smell of three formulations in pellets and plaques

Table 8 shows the list of compounds emitting from the three formulations side by side in pellets.

From Table 8 it can be concluded that four common compounds emitted out of the three pellets. They were:

1. Di-ter -butyl phenol at RT of 9.798
2. Palmitic acid at RT of 13.050
3. Stearic acid at RT of 14.329 and

Table 8 Comparing compounds present in the three new formulated pellets

Table 8	**Comparing compounds present in the three new formulations in pellets**						
Retention Time (mins)	S119346		Retention Time (mins)	S120167		Retention Time (mins)	S120168
9.594	BHT -quinone-methide		2.201	2 - methyl -1 - pentene		2.160	2 - methyl -1 - pentene
9.798	2,4-Di-ter-butylphenol		3.544	2,4 -Dimethyl - 1-heptene		3.527	2,4 -Dimethyl - 1- heptene
13.056	Palmitic acid		4.765	Phenol		4.765	Phenol
14.329	Stearic acid		9.786	2,4-Di-ter-butylphenol		9.594	BHT -quinone-methide
21.429	Tris (2,4-di-ter-butylphenyl)phosphite		9.851	Butylated hydroxytoluene		9.792	2,4-Di-ter-butylphenol
			11.666	Eicosane and octadecene		13.050	Palmitic acid
			13.050	Palmitic acid		14.323	Stearic acid
			14.323	Stearic acid			

4. Butylated hydroxytoluene at RT of 9.594 – It is a primary stabilizer (primary antioxidant). These are classified as hindered phenols. They function as primary antioxidants and act as radical scavengers. Antioxidants prevent oxidation, deterioration, and the release of noxious gases due to uncontrolled oxidation.

The amount of each compound present was quantitated to investigate which formulation had the highest concentration. Since S119346 had the worst smell, it served as the control for the quantitation at concentration of 100%. The other two were quantitated off of this control. Anything less than 100% indicates there is less concentration and anything more than 100% shows that there is more concentration. Figures E.3, E.4 and E.5 in Appendix E show the results of the compound quantitation for S119346, S120167 and S120168 respectively.

The results of the smell test and the quantitation from the GC/MS were compared to help determine the possible cause of smell. Table 9 summarizes the results

Table 9 Comparing smell rating and compounds in the three formulations of pellets

Table 9	COMPARING RESULTS OF COMPOUNDS IN THE THREE NEW FORMULATIONS		
Analysis	S119346	S120167	S120168
Smell Rating	3.8	3.3	3.4
Di-ter -butyl phenol	100%	161%	126%
Palmitic acid	100%	34%	45%
Stearic acid	100%	33%	33%
Butylated Hydroxytoluene	100%	99%	70%

From Table 9 the following observations could be made:

- Although formulations S120167 and S120168 had the best smell, they had higher concentrations of di-ter -butyl phenol. Di-ter -butyl phenol is a derivative of phenol and hence an aromatic smell is expected. It can be deduced that di-ter-butyl phenol is not the only primary cause of smell; other compounds may be possibly contributing to the overall poor smell ratings.
- Lower concentrations of palmitic acid, stearic acid and BHT - quinone –methide were observed in S120167 and S120168

- In addition, if higher concentrations of a compound correlate to bad smell ratings, then palmitic acid, stearic acid may be contributing to smell. This is because higher concentrations were found in S119346 than the other two.

Similar analysis was done on the plaque samples. Table 10 shows the list of compounds emitting from the three formulations side by side in the plaques.

Table 10 Comparing compounds present in the three new formulations in molded plaque

Table 10	**Comparing compounds present in the three new formulations in plaques**						
Retention Time (mins)	S119346		Retention Time (mins)	S120167		Retention Time (mins)	S120168
1.956	Pentane		2.032	Pentane		2.627	2 - methyl -1 - pentene
2.137	2 - methyl -1 - pentene		2.207	2 - methyl -1 - pentene		3.521	2,4 -Dimethyl - 1- heptene
3.509	2,4 -Dimethyl - 1- heptene		3.356	2,4 -Dimethyl - 1- heptene		9.588	Butylated hydroxytoluene
9.507	Butylated hydroxytoluene		4.776	Phenol		13.062	Palmitic acid
9.792	2,4-Di-ter-butylphenol		9.851	Butylated hydroxytoluene		14.335	Stearic acid
13.056	Palmitic acid		12.875	Eicosane			
14.329	Stearic acid		13.062	Palmitic acid			

From Table 10 it can be concluded that several similar compounds present in the three plaques were:

1. 2,4-dimethyl-1-heptene
2. Butylated hydroxytoluene or BHT -Quinone –methide
3. Hexadecanoic acid or palmitic acid
4. Octadecanoic acid or stearic acid and possibly
5. 2-methyl-1-pentene

Hence, the following analysis can be made:

- The only compound present in both plaque S119364 and S120167 that was not present in S120168 was phenol and its derivative phenol, 2,4 - bis (1-1 - dimethylethyl).
- The absence of this compound in S120168 could be a good indicator of why S120168 had a better rating than S119364. The concentrations of stearic acid and palmitic acid in S119364 could also be higher than in the other two plaques.

Comparing Pellets and Plaques for Formulation S120168

The next step was to investigate if there was a significant change in the compounds present after molding. The results of the compounds from the pellet to that of the plaque for formulation S120168 were compared. Figures F.1 and F.2 in Appendix F show the chromatograms comparing S120168 in pellet and plaque. Table 11 shows the list of compounds present in the plaque and pellet formulations.

From Table 11 it can be seen that phenol and di- ter-butylphenol were present in the compounding pellet, but not present in the molded plaque. The possibility is that at high melting temperature during the molding process the heat removed some of the volatile phenols. As a result it was concluded that:

- The molding process can give a different dimension to the final outcome of the product.
- A suggestion to dry the pellets prior to molding at Company B could significantly decrease these volatiles and give better smell outcomes to the final molded polymer.

Table 11 Results of compounds present in pellet and plaque for S120168

Table 11	**Comparing compounds present in pellets and plaque for S120168**			
Retention Time (mins)	S120168 pellet		Retention Time (mins)	S120168 plaque
2.160	2 - methyl -1 - pentene		2.627	2 - methyl -1 - pentene
3.527	2,4 -Dimethyl - 1- heptene		3.521	2,4 -Dimethyl - 1- heptene
4.765	Phenol		9.588	Butylated hydroxytoluene
9.594	BHT -quinone-methide		13.062	Palmitic acid
9.792	2,4-Di-ter-butylphenol		14.335	Stearic acid
13.050	Palmitic acid			
14.323	Stearic acid			

Injection Molding at Company B

At Company B, the pellets from Company A are dried using a carousel dryer at 350^{0}C. This removes the moisture and some volatiles that might be present. Next, the pellets are transferred into the hopper of the injection mold by means of vacuum. The polymer is then softened and conveyed with a screw by pushing through a runner system into a cavity in the tool. Three pressure stages are employed.

The first stage is the pill stage where the melted polymer fills the cavity but not completely. The second is the pack stage which gives it enough pressure just to fill the cavity. The third stage holds the pressure to stabilize the mold and the molded polymer till it solidifies. The molded polymer is then ejected and goes through a conveyer for about 10 seconds to cool. The molded polymer is then inspected and packaged.

At Company B, six different iterations of the final polymer were molded, two for each formulation with the pellets either dried or undried prior to molding. These were then sent to Company C for further analysis. The six iterations were:

1. 1 – 1 – X – Undried molded polymer for lot number S120167
2. 1 – 2 – X – Dried molded polymer for lot number S120167
3. 2 – 1 – X – Undried molded polymer for lot number S119364
4. 2 – 2 – X – Dried molded polymer for lot number S119364
5. 3 – 1 – X – Undried molded polymer for lot number S120168
6. 3 – 2 – X – Dried molded polymer for lot number S120168

Results and Analysis of the Final Molded Polymers at Company C

A blind test of the original problem polymer was conducted along with the newly formulated molded polymers. This way, a fair assessment of whether there had been an improvement from the original problem molded polymer could be determined. Table 12 and Figure 7 show the results of the smell test conducted by eight specialists. It can be said that formulation S120168 had the best overall smell rating. These results and the data clearly show improvement in two of the newly formulated molded polymers from the original molded polymer.

Although it can be said that there had been improvements in the polymer, four hypotheses tests were performed to determine the extent of significant improvement.

1. A hypothesis test at 95 % confidence interval to test if there is significant improvement in the smell of the original molded polymer and the recommended molded polymer formulation –S120168. The one-tailed test yielded a P-value of

0.000166. It can be concluded that there is evidence that there has been significant improvement in the smell of formulation S120168 from the original molded polymer.

2. A hypothesis test at 95 % confidence interval to show that there is no significant difference in smell rating between formulation S120168 and S120167. The two – tailed test yielded a P-value of 0.253852. Hence, it can be concluded that there is sufficient evidence that there is no significant difference in the average smell rating of molded polymers made with formulation S120168 and formulation S120167.
3. A hypothesis test at 95 % confidence interval that there is significant improvement in the smell rating between the original polymer and formulation S119364. The one-tailed test yielded a P-value of 0.04563. It can be concluded that there is not sufficient evidence to support the claim that there is significant improvement in smell between the original molded polymer and that of formulation S119364. Hence, the removal of just the heat aging from the formulation did not improve odor.
4. A hypothesis test at 95% confidence interval that for formulation S120168 there is no difference in the smell rating of molded polymers made from pellets that were dried and pellets that were not dried. The two tailed test resulted in a P-value of 0.465356. It can be concluded that there is sufficient evidence to show that there is no difference in the smell rating of molded polymers made from pellets that were dried and pellets that were not dried for formulation S120168.

Table 12 Smell rating of molded polymer with pellets dried and undried prior to molding

COMPANY C

Table 12	ODOR (SMELL) TEST							
	Jar No.	Interpretation	Participant	Participant Rating	Comments	Participant	Participant Rating	Average
1	SAMPLE A	Original Problem Polymer	1	4.5		6	4.0	4.4
			2	5.0		7	4.5	
			3	4.0		8	4.0	
			4	5.0				
			5	4.0				
2	SAMPLE B	(1-2-8)	1	3.0		6	3.0	3.3
			2	4.0		7	3.0	
			3	3.0		8	3.0	
			4	4.0		9	3.5	
			5	3.0				
3	SAMPLE C	(2-2-8)	1	3.5		6	3.0	3.7
			2	4.0		7	4.0	
			3	3.5		8	4.0	
			4	4.0		9	3.5	
			5	4.0				
4	SAMPLE D	(3-2-10)	1	3.5		6	3.0	3.5
			2	4.5		7	3.5	
			3	3.0		8	3.5	
			4		5.0*			
			5	3.5				
5	SAMPLE E	Original Molded Polymer	1	4.0		6	4.0	4.0
			2	4.0		7	4.0	
			3	4.5		8	3.5	
			4	4.5				
			5	3.5				
6	SAMPLE F	(2-1-9)	1	3.5		6	4.5	3.8
			2	4.0		7	3.5	
			3	3.5		8	3.5	
			4	3.5				
			5	4.0				
7	SAMPLE G	(1-1-8)	1	3.5		6	4.0	3.6
			2	4.5		7	3.0	
			3	3.0		8	4.0	
			4	4.0				
			5	3.0				
8	SAMPLE H	(3-1-7)	1	3.0		6	4.0	3.3
			2	3.5		7	3.0	
			3	3.0		8	4.0	
			4	3.0				
			5	3.0				

Rating Scale :

Grade	Evaluation
1	Not Perceptible
2	Perceptible, not offensive
3	Clearly perceptible, but not yet offensive
4	Offensive
5	Strongly Offensive
6	Unbearable

Comment /Conclusion

The above samples were submitted for a smell test. Some of the samples had their PP pellets dried prior to molding and others did not. The results show that both dried samples 1-2-X and 3-2-X passed the smell test. The undried sample 1-1-X was very close to being in spec. Overall, comparing the original problem molded polymer to our new formulations, we can conclude that there has been significant improvement in the final polymer.

Performed by: Evelyn Lofquist

Standard: Odor ≤ 3.5

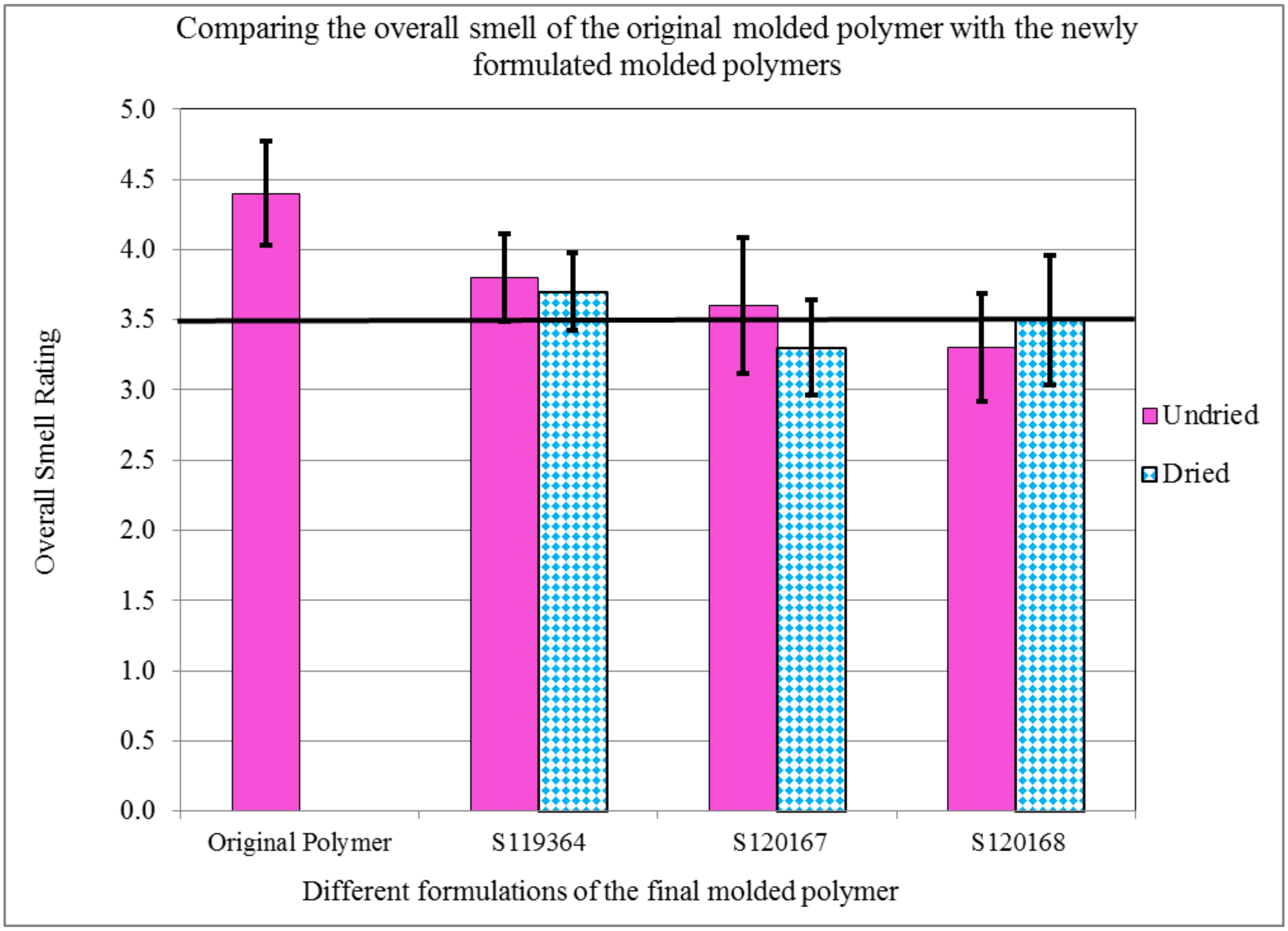

Figure 7 Graph comparing the smell rating of the original molded polymer and the newly formulated polymer.

Additional Analysis—Complete Test Specification

Although the scope of this thesis was limited to smell, in order to suggest which of these formulations to recommend for use in the final product, other tests had to be conducted. This was because at Company C, the smell test is only part of a complete test specification. This test requires that the final molded polymer be tested for smell, fogging, and emissions. Hence a complete test was performed. The final molded polymer that emerged best in all three categories was chosen as the best formulation for the newly molded polymer.

A heat aging test was performed at 150^{0}C for 400 hours and none of the six newly molded polymers showed any sign of degradation. Table 13 shows the compiled results of the overall test according to the complete specifications.

Table 13 Results of the overall test according to the complete specifications

Iterations →	**Original problem polymer**	(2-1-X)	(2-2-X)	(1-1-X)	(1-2-X)	(3-1-X)	(3-2-X)
	Original problem polymer	Formulation 1 Undried	Formulation 1 Dried	Formulation 2 Undried	Formulation 2 Dried	Formulation 3 Undried	Formulation 3 Dried
Smell Test - overall rating (Standard ≤ 3.5)	**4.4**	**3.8**	**3.7**	**3.6**	**3.3**	**3.3**	**3.5**
Fogging Test (Standard : G ≤ 2mg)	**0.3**	**0.3**	**0.2**	**0.2**	**0.0**	**0.2**	**0.0**
Emmission test 1 (Standard ≤ 50µgC/g)	**27.3**	**41.0**	**38.3**	**34.2**	**29.2**	**41.3**	**25.4**
Emmission test 2 (Standard ≤ 50µgC/g)	**29.0**	**37.5**	**36.6**	**35.7**	**28.7**	**41.1**	**25.2**
Emmission test 3 (Standard ≤ 50µgC/g)	**33.7**	**43.8**	**37.5**	**32.2**	**26.7**	**40.9**	**24.5**

From the results above, a hypothesis test at the 95% confidence level was performed. Based on the results of the p-value, the following conclusions were made:

- Drying the pellets prior to molding does not significantly improve the smell of the final molded polymer.
- Drying the pellets prior to molding significantly improved emission values in Formulations 2 and 3 but not in Formulation1.
- It can be seen that iteration 3-2-X passed in all categories of the complete test and hence is the most recommended formulation.

Currently, the newly developed resin has been approved and is in production.

CHAPTER V

CONCLUSIONS

- A generalized process was developed to resolve odor issues in molded polymers as seen in Appendix F.
- There was significant improvement in smell in the final chosen formulated polymer compared to the original.
- There was no significant difference in the smell rating between formulation S120167 and S120168. Hence, should Company B encounter any issues during the molding process of S120168, S120167 can be used as a substitute.
- In general, drying the pellets prior to molding does not impart smell, but may produce significant improvements in other specifications such as emissions.
- In analyzing the possible cause of smell using the GC/MS, odiferous compounds were found as seen in Appendix K.
- An assumption of a compound possibly contributing to odor was based on the knowledge of the general behaviors for compounds within specific functional groups.
- It is important to note that these assumptions are not conclusive and are not proof that the presence of these compounds caused the specific odors identified by the panel.

Recommendation

For further investigation into the distinct smell of these compounds and if such a smell leads to a poor rating of the final polymer, pure samples of each of these compounds will have to be purchased. Each compound will have to be tested and a personal library built into the database of Company C’s GC/MS for reference. This will assist in the easy identification of similar odors from other future molded polymers

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APPENDIX A

RESULTS OF INITIAL SMELL TEST ON INDIVIDUAL INGREDIENTS AND RESIN

Table A.1 Smell tests of the individual compounding ingredients

COMPANY C

Table A.1	ODOR (SMELL) TEST							
	Resin/Additives	Participant	Participant Rating	Comments	Participant	Participant Rating	Comments	Average
1	Resin	1	3.5	yeast	6	3.0		3.3
		2	3.5	Waxy	7	3.5		
		3	3.5		8	3.0		
		4	4.0	burnt				
		5	2.5					
2	Talc	1	3.0	Flour	6	2.0		2.6
		2	2.0	talc powder	7	3.0		
		3	2.5		8	3.0		
		4	2.0	OK				
		5	3.0					
3	Color	1	4.0	Old smell	6	4.5		4.0
		2	4.5	Burnt plastic	7	4.0		
		3	3.5		8	3.0		
		4	4.0	Burnt				
		5	4.5	Burned Oil				
4	Lubricant	1	3.5	Smell of Vinegar	6	3.0		3.8
		2	4.0	Sweet Smell	7	4.0		
		3	3.5		8	4.0	Musk	
		4	4.0	Vinegar				
		5	4.5	Sugar				
5	Heating Agent (DSTDP)	1	4.0	Vinegar	6		Rating : 2.5	4.1
		2	4.0	Rancid Smell	7	4.0		
		3	3.0		8	4.0	Sweet	
		4	4.0	Sharp				
		5	5.5	Phenol, solvent aromatic				
6	Heating Agent (Epoxy)	1	2.5		6	3.0		3.3
		2	3.5	Sweet	7	3.5		
		3	3.0		8	4.0	Musk	
		4	3.0	OK				
		5	3.5					

	Rating Scale :			
	Grade		Evaluation	The above resin and additives were submitted for a smell test according to standards. Lubricant, color and DSTDP are Not OK since they do not meet specifications
	1		Not Perceptible	
	2		Perceptible, not offensive	
	3		Clearly perceptible, but not yet offensive	
	4		Offensive	
	5		Strongly Offensive	Standard: Odor $\leq$ 3.5
	6		Unbearable	

COMPANY C

Table A.1 Cont.	ODOR (SMELL) TEST							
	Additive	Participant	Participant Rating	Comments	Participant	Participant Rating	Comments	Average
7	Stripping Agent	1	3.0		6	2.0		2.8
		2	2.0		7	3.5		
		3	3.0	Wet	8	3.0		
		4	3.0					
		5	3.0					
8	Final Product	1	4.0	Moldy	6	3.5		4.3
		2	5.0	Burnt Plastic	7	4.0		
		3	4.0		8	4.0	Musk	
		4	5.0	Burnt Plastic				
		5	4.5					
9	Low Odor Talc	1	4.0	Solvent	6	2.5		3.4
		2	3.5		7	4.0		
		3	3.0		8	3.0		
		4	3.0					
		5	4.0	Grease				
10	Old Resin (From March)	1	3.0		6	2.5		2.9
		2	3.5		7	3.5		
		3	3.0		8	3.0		
		4	2.0					
		5		4.5 Musty				
	Rating Scale :							
	Grade		Evaluation		The above additives and PP pellets were submitted for a smell test according to standards. Clearly, the final PP product is Not OK due to odor failure			
	1		Not Perceptible					
	2		Perceptible, not offensive					
	3		Clearly perceptible, but not yet offensive					
	4		Offensive					
	5		Strongly Offensive		Standard: Odor ≤ 3.5			
	6		Unbearable					
	Performed by: Evelyn Lofquist							

APPENDIX B

METHODOLOGY FOR ANALYZING COMPOUNDS

EGA thermogram and chromatogram for color

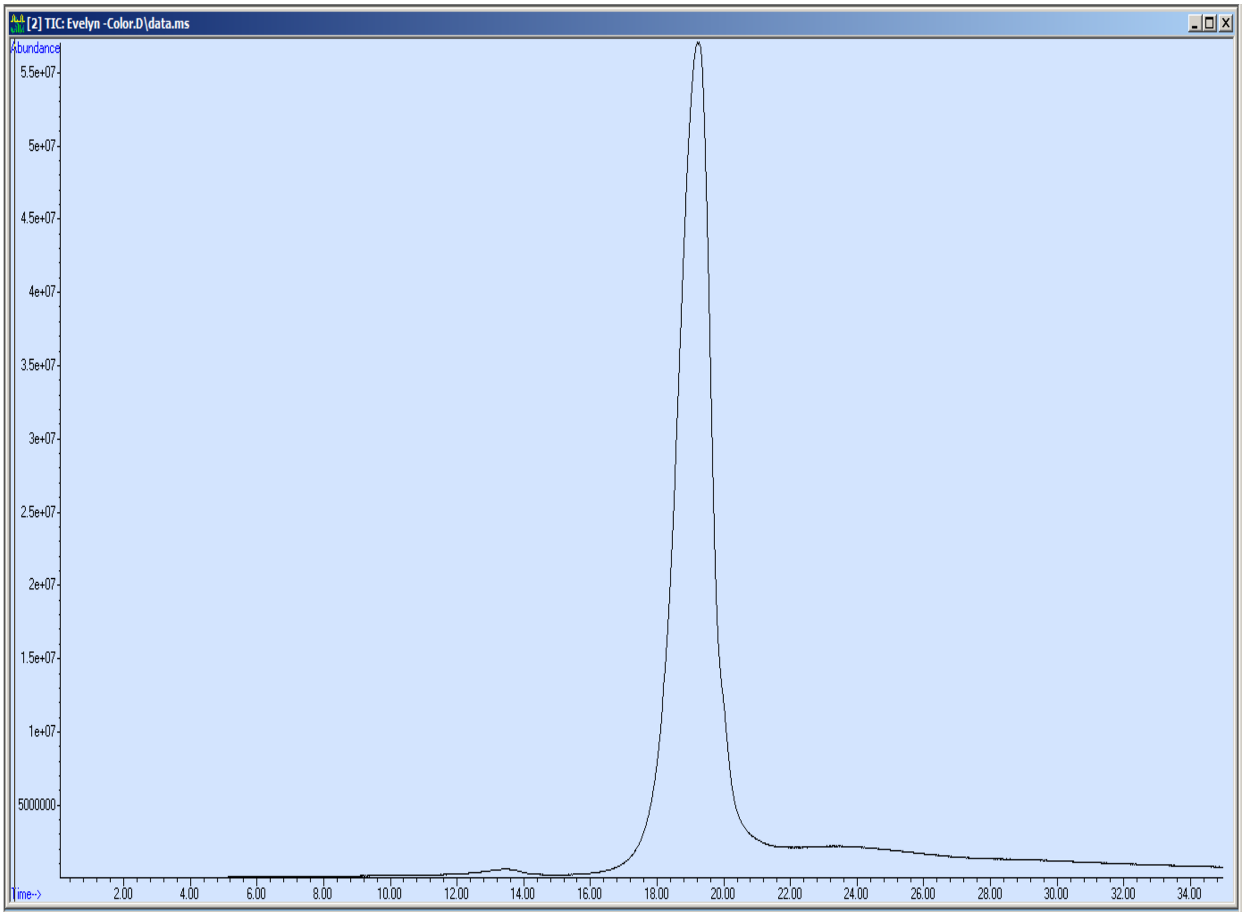


Figure B.1 Thermogram of EGA analysis for color additive.

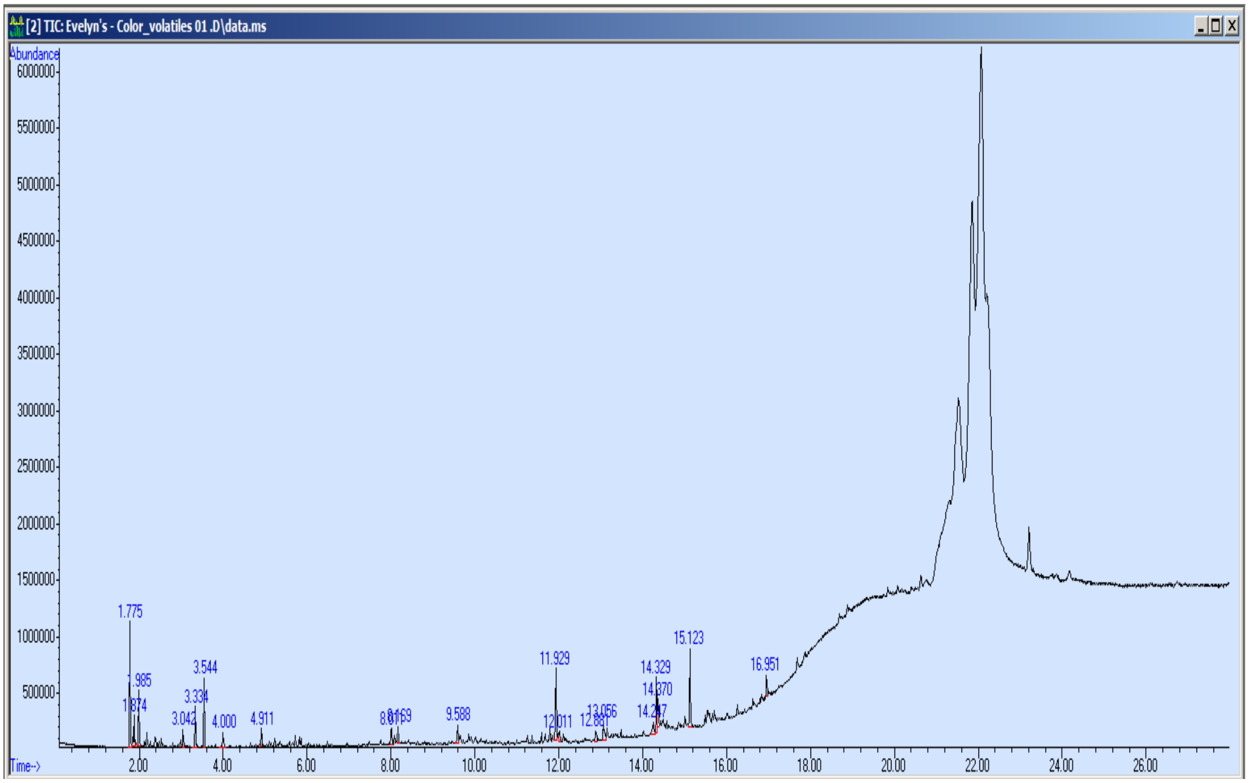
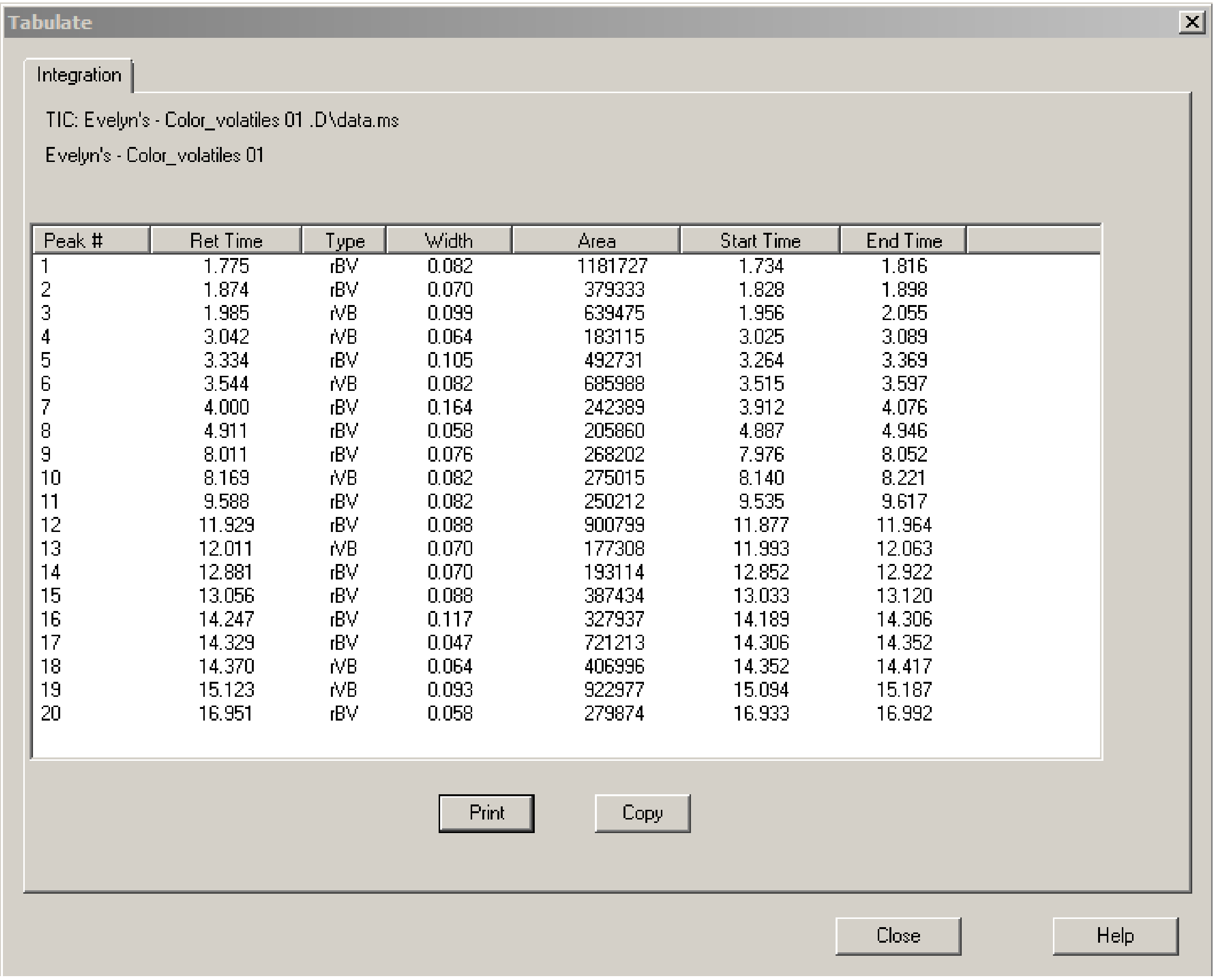


Figure B.2 Total ion chromatogram for the thermodesorption portion of the color additive.

Steps for analyzing the chromatograms using color as an example.

In analyzing the chromatograms, two different library searches were used. These are the NIST library and the F-Search library. The following steps were used in analyzing the chromatograms and determining what compounds were actually being emitted from each additive using the NIST library.

1. The peaks were integrated and the retention times were noted as seen in Figure B.3.
2. The corresponding compounds and their respective percentage quality matches were also noted. A quality match closer to 100% assumes the peak to be a good match as seen in Figure B.4.

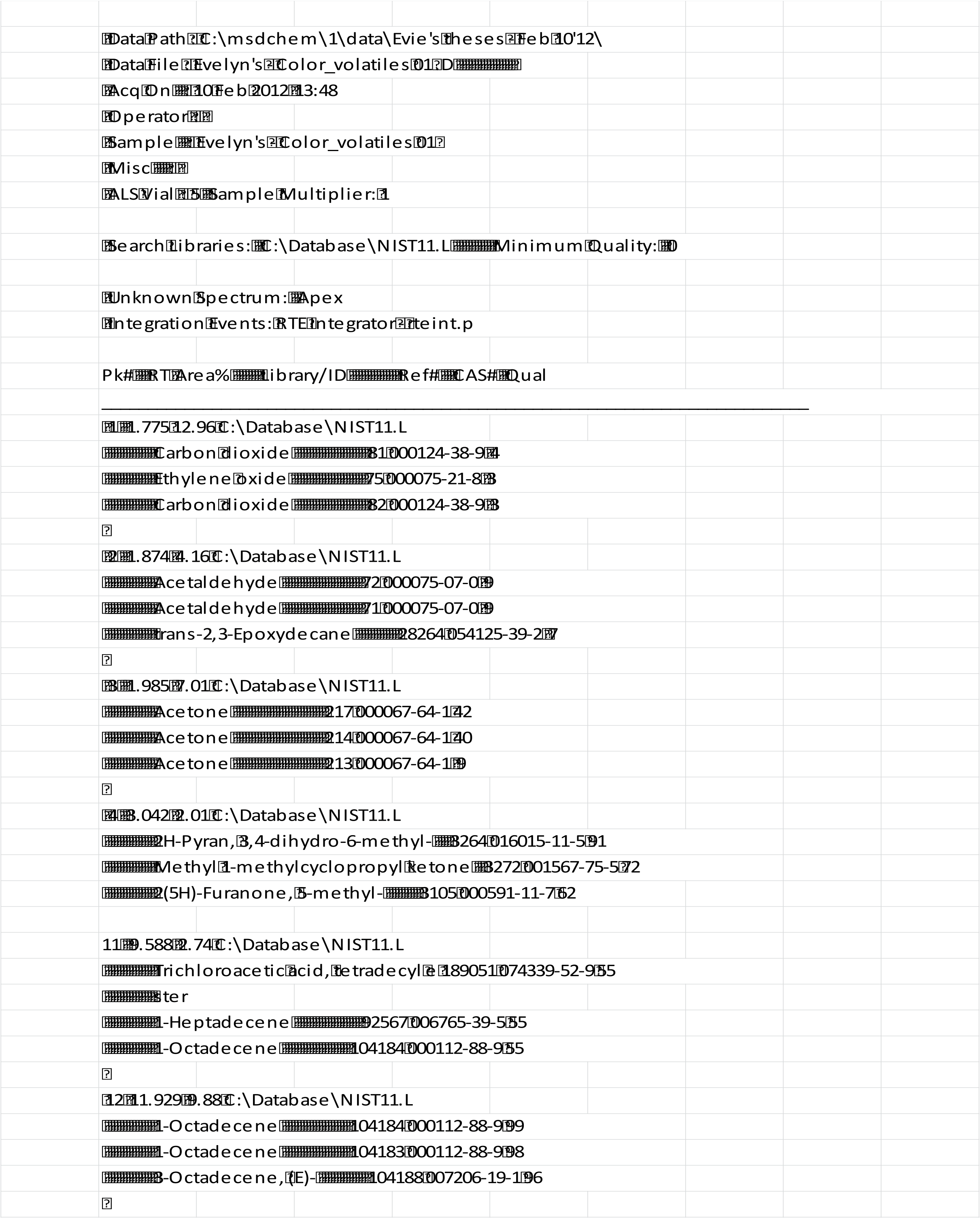


TIC: Evelyn's - Color_volatiles 01 .D\data.ms

Evelyn's - Color_volatiles 01

Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	1.775	rBV	0.082	1181727	1.734	1.816
2	1.874	rBV	0.070	379333	1.828	1.898
3	1.985	rVB	0.099	639475	1.956	2.055
4	3.042	rVB	0.064	183115	3.025	3.089
5	3.334	rBV	0.105	492731	3.264	3.369
6	3.544	rVB	0.082	685988	3.515	3.597
7	4.000	rBV	0.164	242389	3.912	4.076
8	4.911	rBV	0.058	205860	4.887	4.946
9	8.011	rBV	0.076	268202	7.976	8.052
10	8.169	rVB	0.082	275015	8.140	8.221
11	9.588	rBV	0.082	250212	9.535	9.617
12	11.929	rBV	0.088	900799	11.877	11.964
13	12.011	rVB	0.070	177308	11.993	12.063
14	12.881	rBV	0.070	193114	12.852	12.922
15	13.056	rBV	0.088	387434	13.033	13.120
16	14.247	rBV	0.117	327937	14.189	14.306
17	14.329	rBV	0.047	721213	14.306	14.352
18	14.370	rVB	0.064	406996	14.352	14.417
19	15.123	rVB	0.093	922977	15.094	15.187
20	16.951	rBV	0.058	279874	16.933	16.992

Figure B.3 Integrated peaks and retention time table for color.

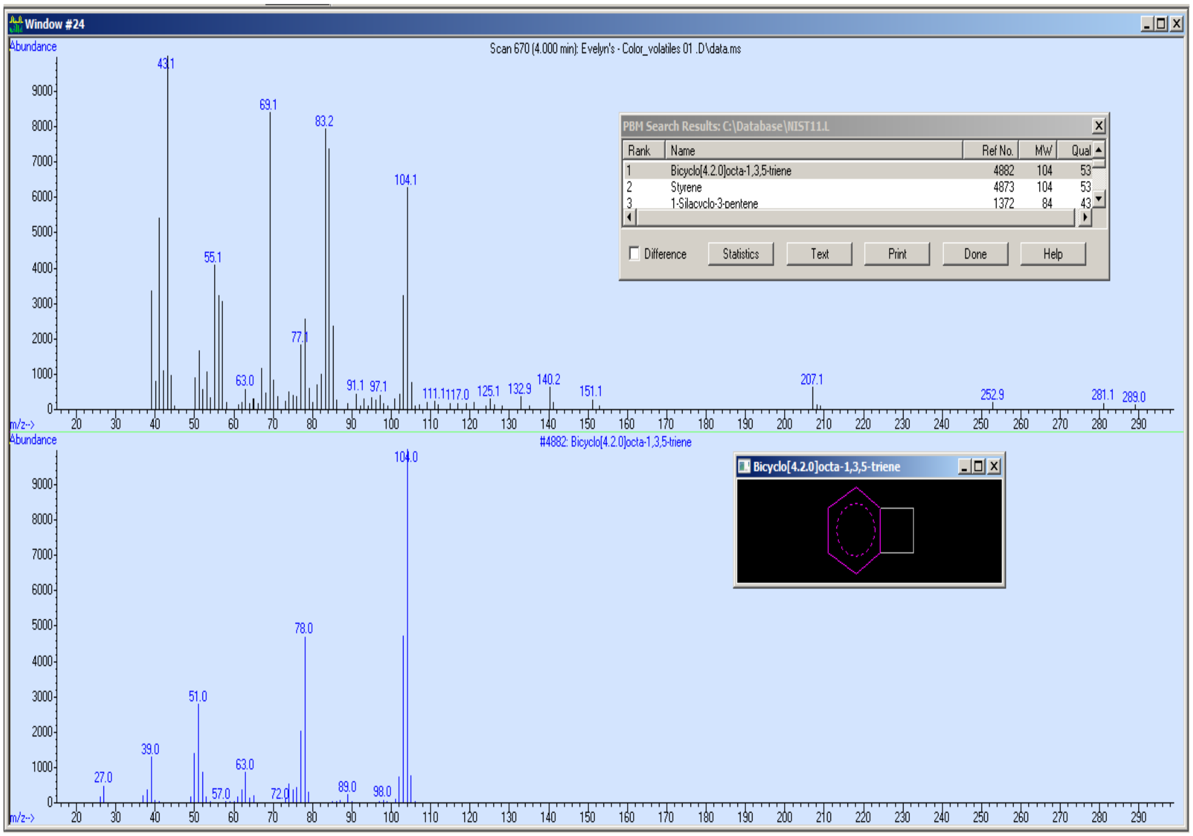


```
 Data Path : C:\msdchem\1\data\Evie's theses  Feb 10'12\
 Data File : Evelyn's  Color_volatiles 01 D
 Acq On    : 10 Feb 2012  13:48
 Operator  :
 Sample    : Evelyn's  Color_volatiles 01
 Misc      :
 ALS Vial  : 5  Sample Multiplier: 1

 Search Libraries:  C:\Database\NIST11.L          Minimum Quality: 0

 Unknown Spectrum:  Apex
 Integration Events: RTE Integrator  rteint.p

Pk#  RT  Area%      Library/ID          Ref#  CAS#  Qual
______________________________________________________________________________
 1  1.775 12.96 C:\Database\NIST11.L
          Carbon dioxide                 81 000124-38-9  4
          Ethylene oxide                 75 000075-21-8  3
          Carbon dioxide                 82 000124-38-9  3

 2  1.874  4.16 C:\Database\NIST11.L
          Acetaldehyde                   72 000075-07-0  9
          Acetaldehyde                   71 000075-07-0  9
          trans-2,3-Epoxydecane       28264 054125-39-2  7

 3  1.985  7.01 C:\Database\NIST11.L
          Acetone                       217 000067-64-1 42
          Acetone                       214 000067-64-1 40
          Acetone                       213 000067-64-1  9

 4  3.042  2.01 C:\Database\NIST11.L
          2H-Pyran, 3,4-dihydro-6-methyl-    3264 016015-11-5 91
          Methyl 1-methylcyclopropyl ketone  3272 001567-75-5 72
          2(5H)-Furanone, 5-methyl-     3105 000591-11-7 62

11  9.588  2.74 C:\Database\NIST11.L
          Trichloroacetic acid, tetradecyl e 189051 074339-52-9 55
          ster
          1-Heptadecene               92567 006765-39-5 55
          1-Octadecene               104184 000112-88-9 55

 12 11.929  9.88 C:\Database\NIST11.L
          1-Octadecene               104184 000112-88-9 99
          1-Octadecene               104183 000112-88-9 98
          3-Octadecene, (E)-         104188 007206-19-1 96

```

Figure B.4 Results of percentage quality match to their compounds for old color additive.

For this example, the preliminary results indicate that the quality match of 1-octadecene at a retention time of 11.929 is 99%. For now, 1-octadecene will be considered as a compound present in the color additive.

3. Next, the number of peaks to further investigate is narrowed down by eliminating peaks with lower percentage quality. Figure B.5 shows a mass spectrum of a bad quality matched peak. Table B.1 shows a list of compounds remaining after elimination that require further analysis.



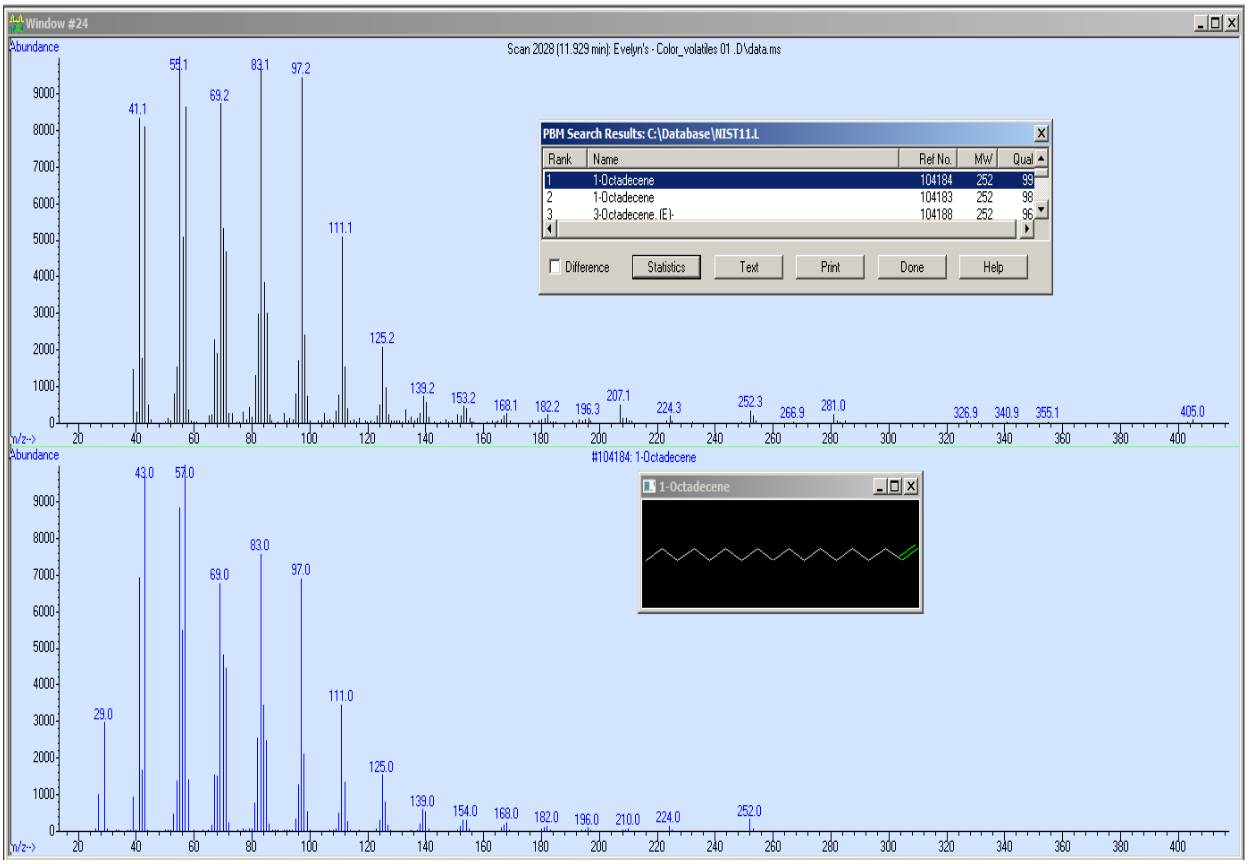
Rank	Name	Ref No.	MW	Qual
1	Bicyclo[4.2.0]octa-1,3,5-triene	4882	104	53
2	Styrene	4873	104	53
3	1-Silacyclo-3-pentene	1372	84	43

Figure B.5 Mass spectrum of styrene at RT of 4.0 with a 53% quality match.

Table B.1 List of compounds remaining after bad quality match elimination

Table B.1	GC/MS COMPILED RESULTS FROM LIBRARY SEARCH FOR COLOR		
Peak No.	Retention Time (mins)	Library/ID	Quality Match
1	3.042	2-H Pyran, 3,4 - dihydro - 6 - methyl-	91%
2	3.544	2,4 - Dimethyl - 1- heptene	90%
3	11.929	1- Octadecene	99%
5	12.011	5 - Octadecen, (E) -	94%
6	12.881	Eicosane	89%
7	13.056	Octadecanoic acid	90%
8	14.329	Octadecanoic acid	99%
9	14.370	Pyrene	95%
10	22.066	Distearyl-3,3'-thiodipropionate	85%

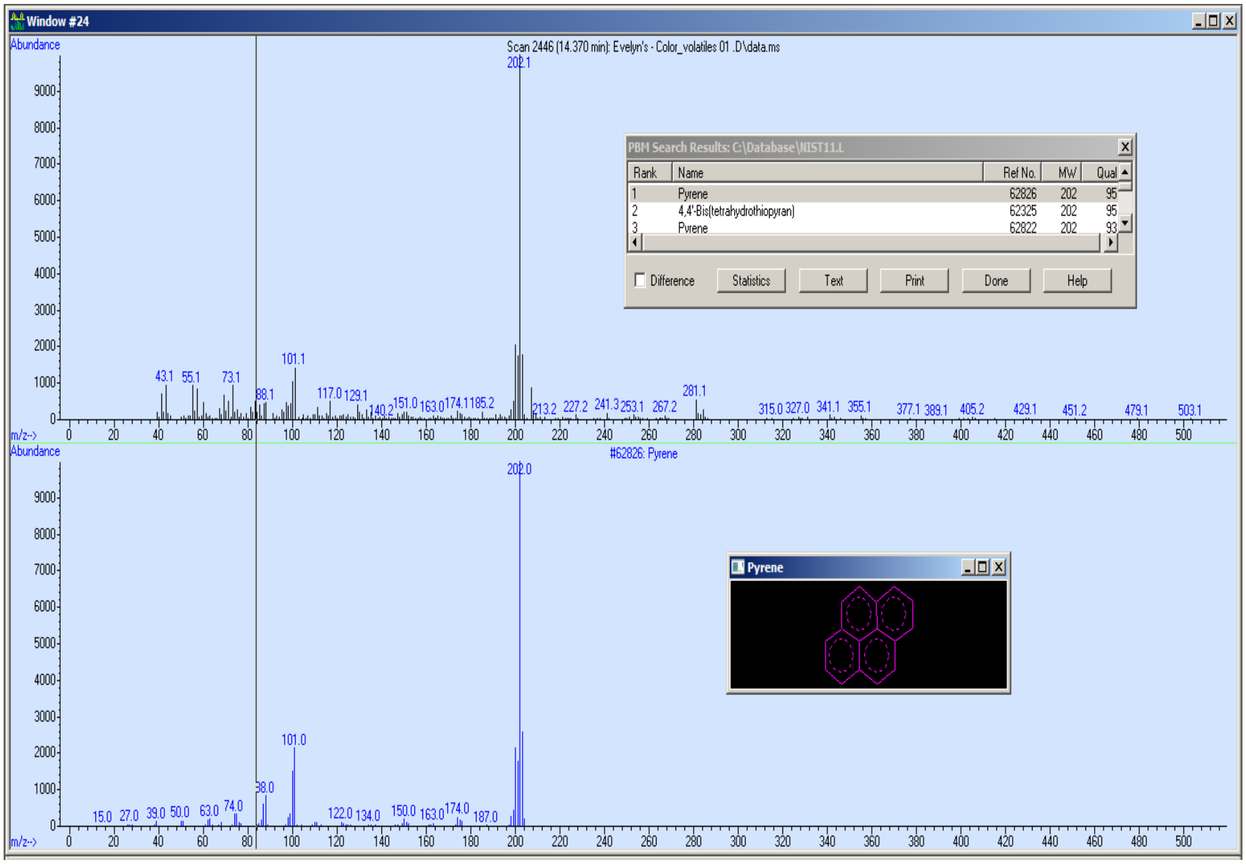
4. Next the spectrum of each compound is visually analyzed by comparing it to the spectra in the NIST search library. If almost all the ions in our compound match that in the library, the compound is considered a good match. For this example, 1-octadecene is considered to be a good a match. Figure B.6 shows the mass spectra for 1-octadecene at a retention time of 11.929.
5. Spectrums that don’t show good spectral matches are further analyzed. Figure B.7 shows mass spectra for pyrene at a RT of 14.370.



PBM Search Results: C:\Database\NIST11.L

Rank	Name	Ref No.	MW	Qual
1	1-Octadecene	104184	252	99
2	1-Octadecene	104183	252	98
3	3-Octadecene, (E)-	104188	252	96

Figure B.6 Mass spectra of 1-octadecene.


Scan 2446 (14.370 min): Evelyn's - Color_volatiles 01 .D\data.ms

#62826: Pyrene

PBM Search Results: C:\Database\NIST11.L

Rank	Name	Ref No.	MW	Qual
1	Pyrene	62826	202	95
2	4,4'-Bis(tetrahydrothiopyran)	62325	202	95
3	Pyrene	62822	202	93

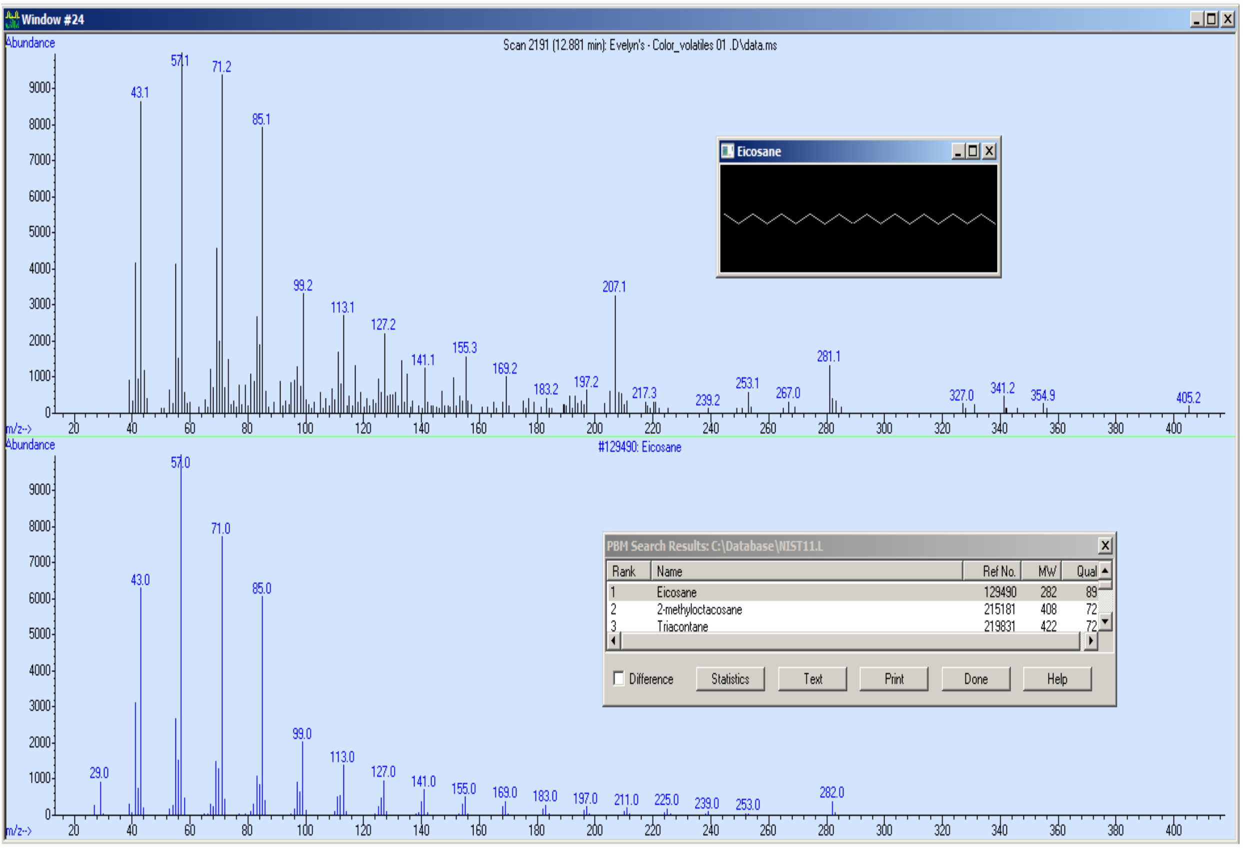
Figure B.7 Mass spectra of pyrene.

Here some ions present in the additive are missing from the spectrum of the compounds in the search library. To determine if those ions are of any importance to the spectra, the molecular weight of the matched compound is compared to the molecular weight of the missing ion. Since the molecular mass of 202 is present in the library and the preceding ions all match, the molecular weight of 281 in the spectrum can be considered as an impurity and hence it can be concluded that we have a good match and compound pyrene is present in the additive.

6. Sometimes, not all high percentage quality match peaks are good. An example is the compound eicosane at RT of 12.881. Although the search yielded an 89% quality match,

a look at the mass spectra says otherwise. Hence it be cannot concluded that eicosane is present. Figure B.8 illustrates this very well.

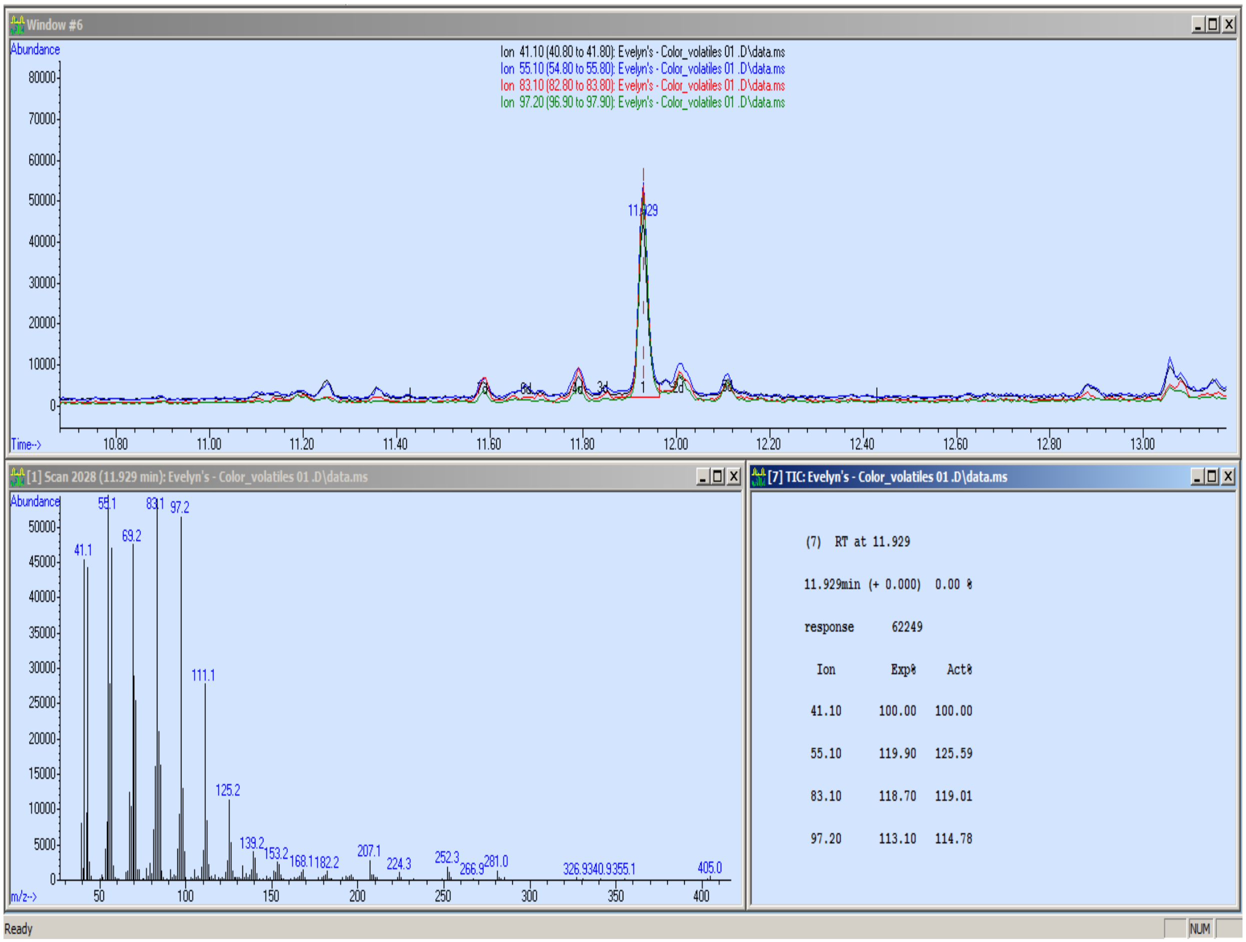
7. Finally, those compounds with good spectral matches were qualitatively analyzed using the Q-editor function in chemstation. This editor analyzes each individual ion that makes up the Total Ion Chromatogram (TIC). If the individual ions analyzed fall under the broad peak, then there is an indication of a good peak. If not, then the reverse is true. Figure B.9 shows an example of such analysis and what it is supposed to look like.
8. Figure B.10 shows an example of a peak with a good percentage quality match but an in depth analysis of the peaks show that it is actually a bad one.
9. Table B.2 shows a result of compounds present in color from the NIST library search



PBM Search Results: C:\Database\NIST11.L

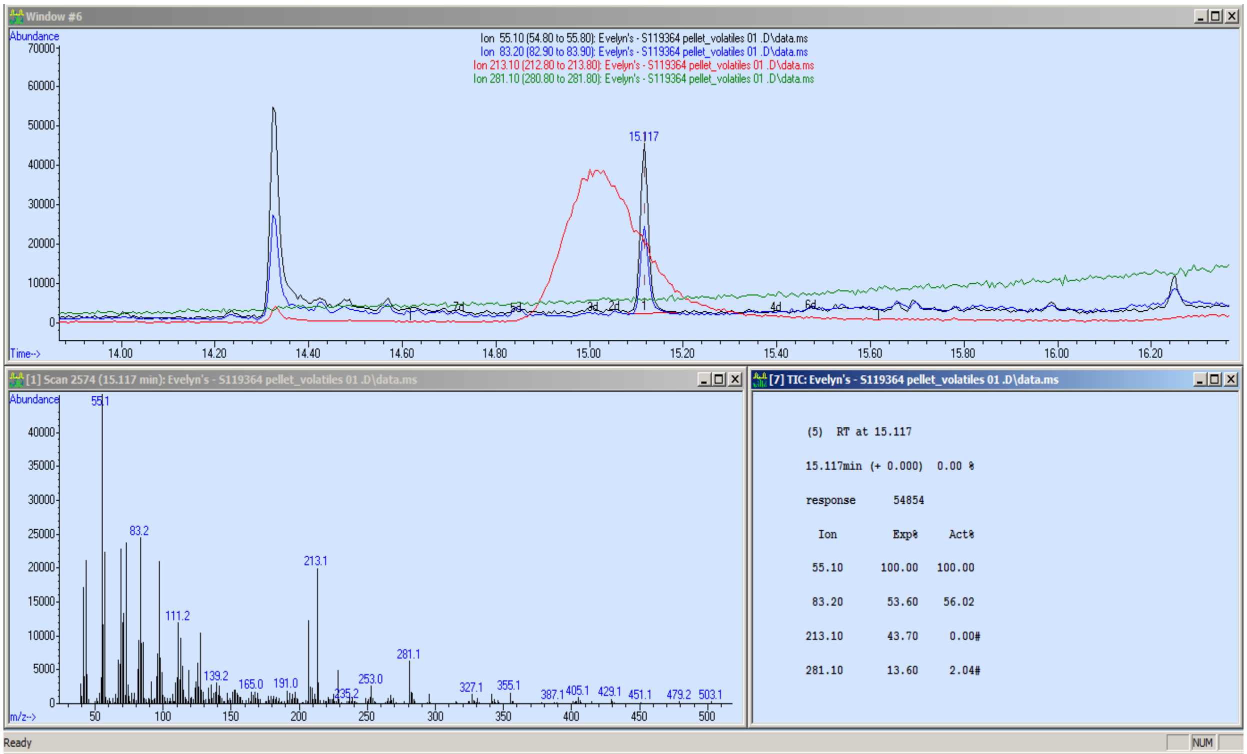
Rank	Name	Ref No.	MW	Qual
1	Eicosane	129490	282	89
2	2-methyloctacosane	215181	408	72
3	Triacontane	219831	422	72

Figure B.8 Mass spectra of eicosane.



```
(7)  RT at 11.929

11.929min (+ 0.000)  0.00 %

response     62249

 Ion       Exp%     Act%

 41.10    100.00   100.00

 55.10    119.90   125.59

 83.10    118.70   119.01

 97.20    113.10   114.78
```

Figure B.9 Qualitative analysis of good peak, 1-octadecene at RT of 11.929.



```
(5)  RT at 15.117

15.117min (+ 0.000)  0.00 %

response      54854

  Ion         Exp%     Act%

 55.10      100.00   100.00

 83.20       53.60    56.02

213.10       43.70     0.00#

281.10       13.60     2.04#
```

Figure B.10 Qualitative analysis of a bad peak at RT of 15.117.

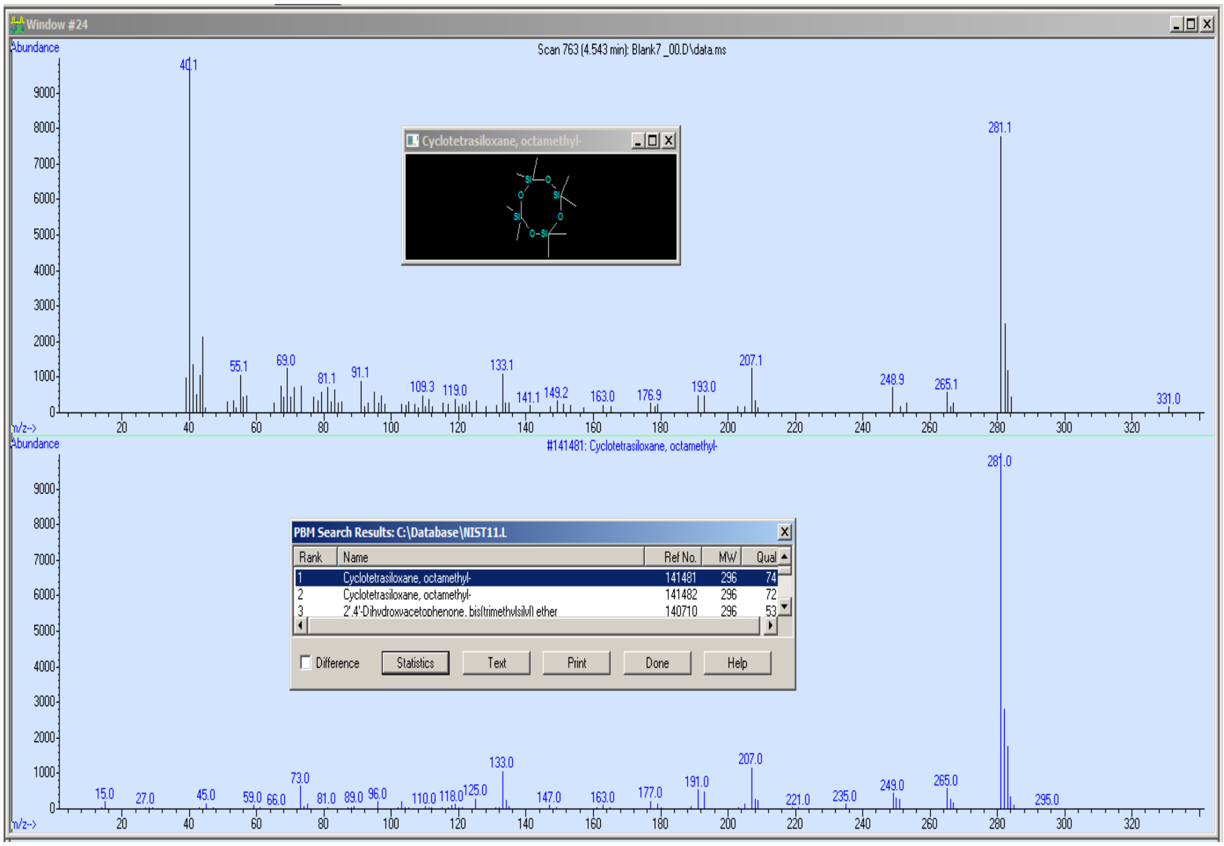
Table B.2 GC/MS result of compounds from NIST library search for color

Table B.2	GC/MS COMPILED RESULTS FROM LIBRARY SEARCH FOR COLOR		
Peak No.	Retention Time (mins)	Library/ID	Quality Match
1	3.042	2-H Pyran, 3,4 - dihydro - 6 - methyl-	91%
2	3.544	2,4 - Dimethyl - 1- heptene	90%
3	11.929	1- Octadecene	99%
5	12.011	5 - Octadecen, (E) -	94%
6	12.881	Eicosane	89%
7	13.056	Octadecanoic acid	90%
8	14.329	Octadecanoic acid	99%
9	14.370	Pyrene	95%
10	22.066	Distearyl-3,3'-thiodipropionate	85%

APPENDIX C

ANALYSIS OF BLANK SAMPLES, NEW AND OLD COLOR ADDITIVES

Figure C.1 shows the mass spectra of siloxanes found in the blank.



PBM Search Results: C:\Database\NIST11.L

Rank	Name	Ref No.	MW	Qual
1	Cyclotetrasiloxane, octamethyl-	141481	296	74
2	Cyclotetrasiloxane, octamethyl-	141482	296	72
3	2',4'-Dihydroxyacetophenone, bis(trimethylsilyl) ether	140710	296	53

Figure C.1 Mass spectrum showing the presence of cyclosiloxane in a blank sample.

Table C.1 shows the results from analysis using NIST and F-search for color.

Table C.1 List of compounds found to be present in both the NIST and F-search libraries

Table C.1	GC/MS NIST LIBRARY SEARCH RESULTS FOR COLOR ADDITIVE			F- SEARCH LIBRARY RESULTS FOR COLOR ADDITIVE			
Peak No.	Retention Time (Mins)	Library/ID	Quality Match	Peak No.	Retention Time	Library/ID	Quality Match
4	3.042	2-H Pyran, 3,4 - dihydro - 6 - methyl-	91%	4	3.544	2,4-Dimethyl -1 -heptene	94%
5	3.334	Cyclotetrasiloxane, octamethyl-	91%	12	11.929	1-Nonadecene	98%
6	3.544	2,4 - Dimethyl - 1- heptene	90%	17	14.329	Stearic acid	93%
8	4.911	Cyclotrisiloxane, octamethyl	91%	8	21.855	Distearyl-3,3'-thiodipropionate	78%
12	11.929	1- Octadecene	99%	22	22.066	Distearyl-3,3'-thiodipropionate	85%
13	12.011	5 - Octadecen, (E) -	94%				
14	12.881	Eicosane	89%				
15	13.056	Octadecanoic acid	90%				
17	14.329	Octadecanoic acid	99%				
18	14.370	Pyrene	95%				

Figure C.2 show the results of the chromatographs of the new color additive P7D.

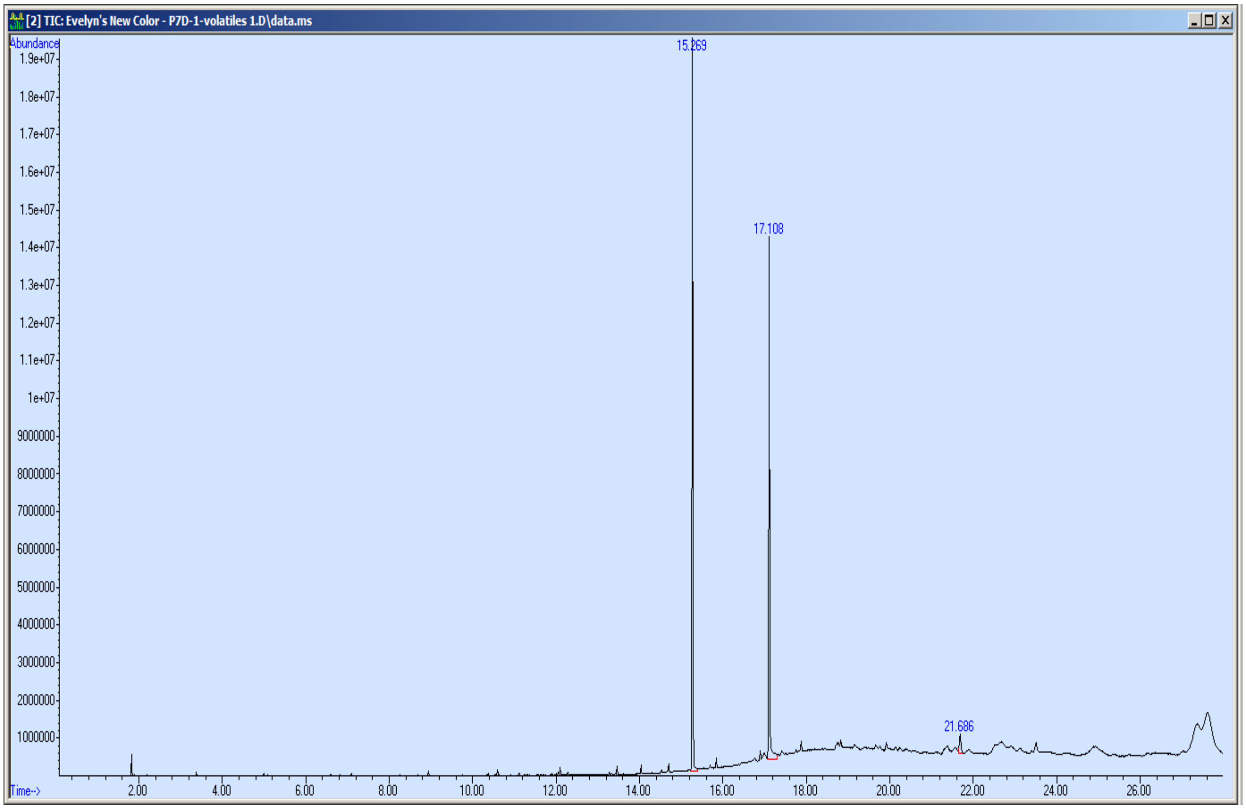
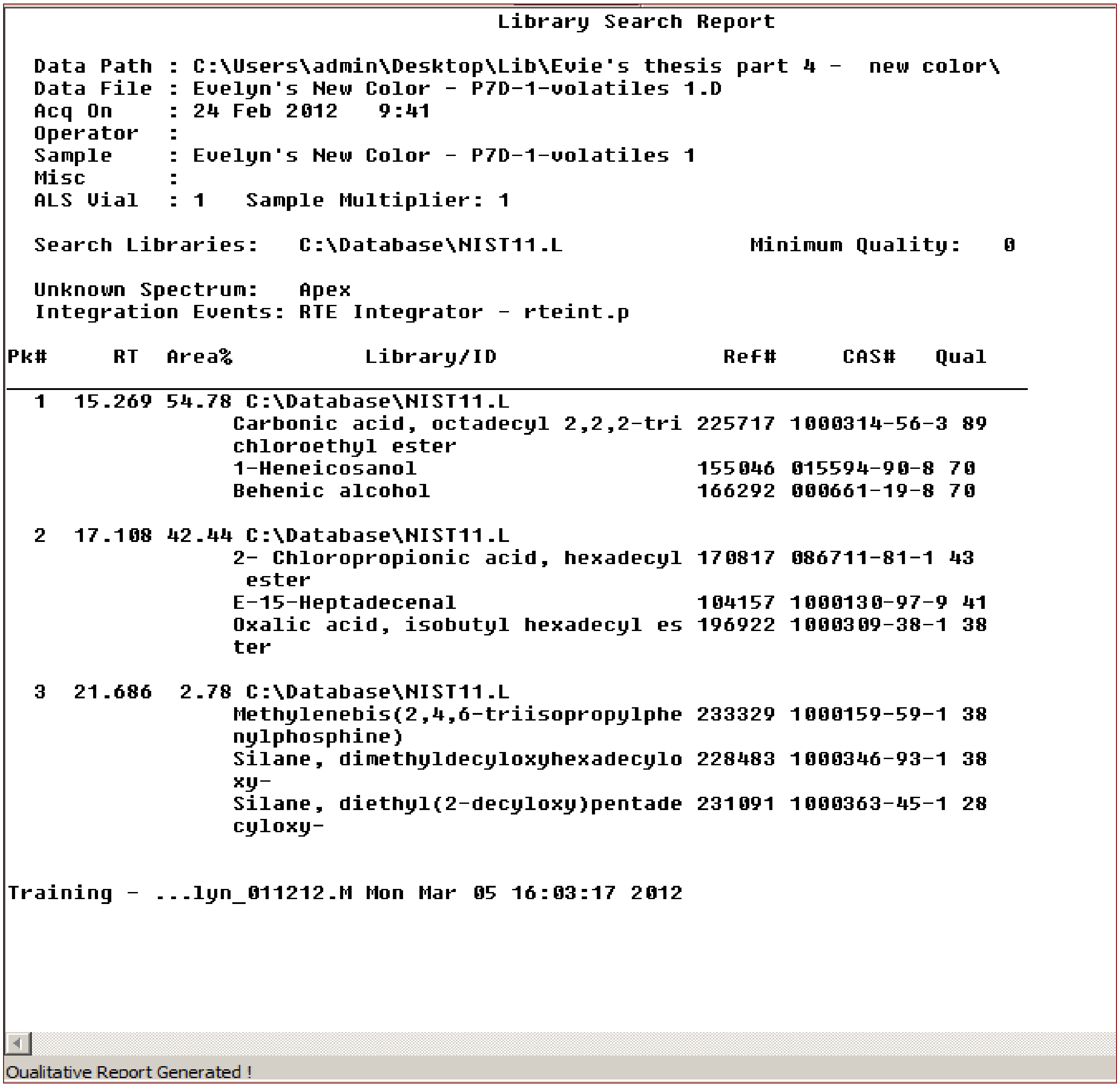


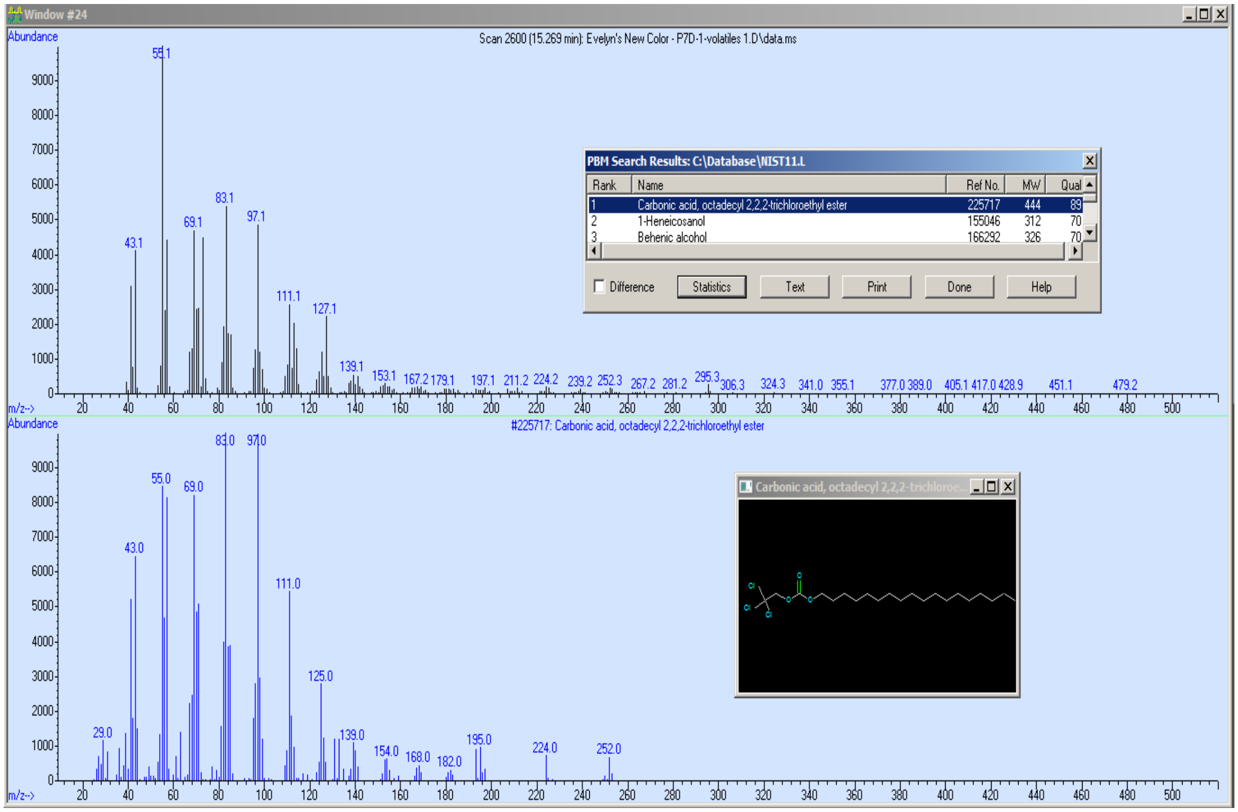
Figure C.2 Chromatograph of new color additive (P7D).

Results for the corresponding compounds and their respective percentage quality matches are shown in Figure C.3. From the results, only the compound carbonic acid, octadecyl 2, 2, 2 – tri chloroethyl ester has a high quality match. Therefore, further analysis was done by matching its spectra to that in the library. Figure C.4 shows the mass spectra of this compound. Comparing the mass spectra to that in the library indicates that this compound is not a good match. Thus an in – depth qualitative analysis of this compound was performed. Figure C.5 shows the results of this analysis.



```
                              Library Search Report

  Data Path : C:\Users\admin\Desktop\Lib\Evie's thesis part 4 -  new color\
  Data File : Evelyn's New Color - P7D-1-volatiles 1.D
  Acq On    : 24 Feb 2012   9:41
  Operator  :
  Sample    : Evelyn's New Color - P7D-1-volatiles 1
  Misc      :
  ALS Vial  : 1   Sample Multiplier: 1

  Search Libraries:   C:\Database\NIST11.L              Minimum Quality:   0

  Unknown Spectrum:   Apex
  Integration Events: RTE Integrator - rteint.p

Pk#     RT  Area%          Library/ID                 Ref#     CAS#   Qual
______________________________________________________________________________
  1  15.269 54.78 C:\Database\NIST11.L
                 Carbonic acid, octadecyl 2,2,2-tri 225717 1000314-56-3 89
                 chloroethyl ester
                 1-Heneicosanol                     155046 015594-90-8 70
                 Behenic alcohol                    166292 000661-19-8 70

  2  17.108 42.44 C:\Database\NIST11.L
                 2- Chloropropionic acid, hexadecyl 170817 086711-81-1 43
                  ester
                 E-15-Heptadecenal                  104157 1000130-97-9 41
                 Oxalic acid, isobutyl hexadecyl es 196922 1000309-38-1 38
                 ter

  3  21.686  2.78 C:\Database\NIST11.L
                 Methylenebis(2,4,6-triisopropylphe 233329 1000159-59-1 38
                 nylphosphine)
                 Silane, dimethyldecyloxyhexadecylo 228483 1000346-93-1 38
                 xy-
                 Silane, diethyl(2-decyloxy)pentade 231091 1000363-45-1 28
                 cyloxy-


Training - ...lyn_011212.M Mon Mar 05 16:03:17 2012
```

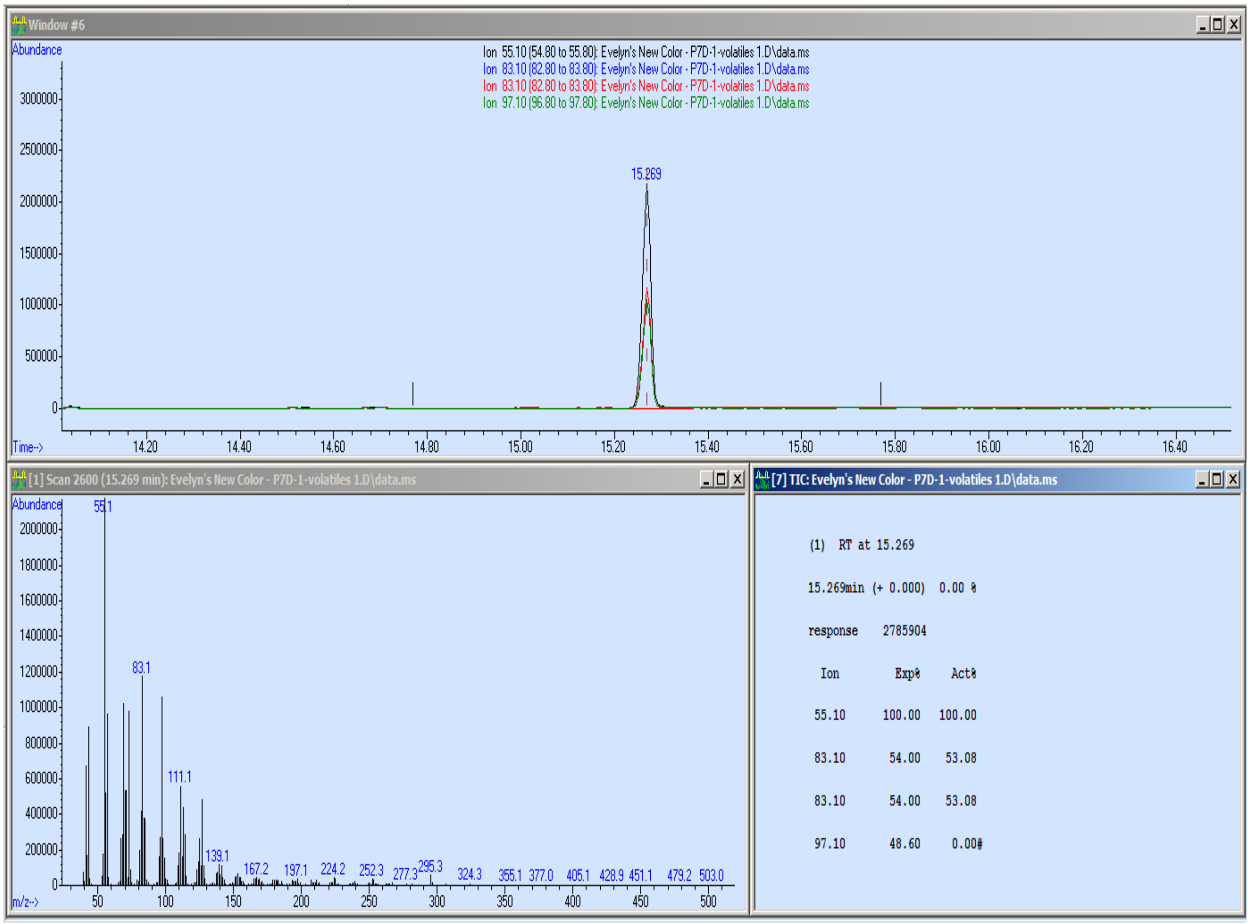
Figure C.3 Compounds from new color additive (P7D) and their quality matches.



PBM Search Results: C:\Database\NIST11.L

Rank	Name	Ref No.	MW	Qual
1	Carbonic acid, octadecyl 2,2,2-trichloroethyl ester	225717	444	89
2	1-Heneicosanol	155046	312	70
3	Behenic alcohol	166292	326	70

Figure C.4 Mass spectra of compound at RT of 15.269.



```
Ion  55.10 (54.80 to 55.80): Evelyn's New Color - P7D-1-volatiles 1.D\data.ms
Ion  83.10 (82.80 to 83.80): Evelyn's New Color - P7D-1-volatiles 1.D\data.ms
Ion  83.10 (82.80 to 83.80): Evelyn's New Color - P7D-1-volatiles 1.D\data.ms
Ion  97.10 (96.80 to 97.80): Evelyn's New Color - P7D-1-volatiles 1.D\data.ms
```

```
(1)  RT at 15.269

15.269min (+ 0.000)  0.00 %

response    2785904

 Ion        Exp%    Act%

 55.10     100.00  100.00

 83.10      54.00   53.08

 83.10      54.00   53.08

 97.10      48.60    0.00#
```

Figure C.5 Q- Edit analysis of carbonic acid, octadecyl 2, 2, 2 – tri chloroethyl ester.

From figure C.6, there is a clear indication that the peak is of a good quality. But since the spectra do not indicate that it is an ester, the certainty of this compound is unknown. It would be safe to say that barely any compounds are being emitted from the new color additive.

Figure C.6 compares both color additives side by side.

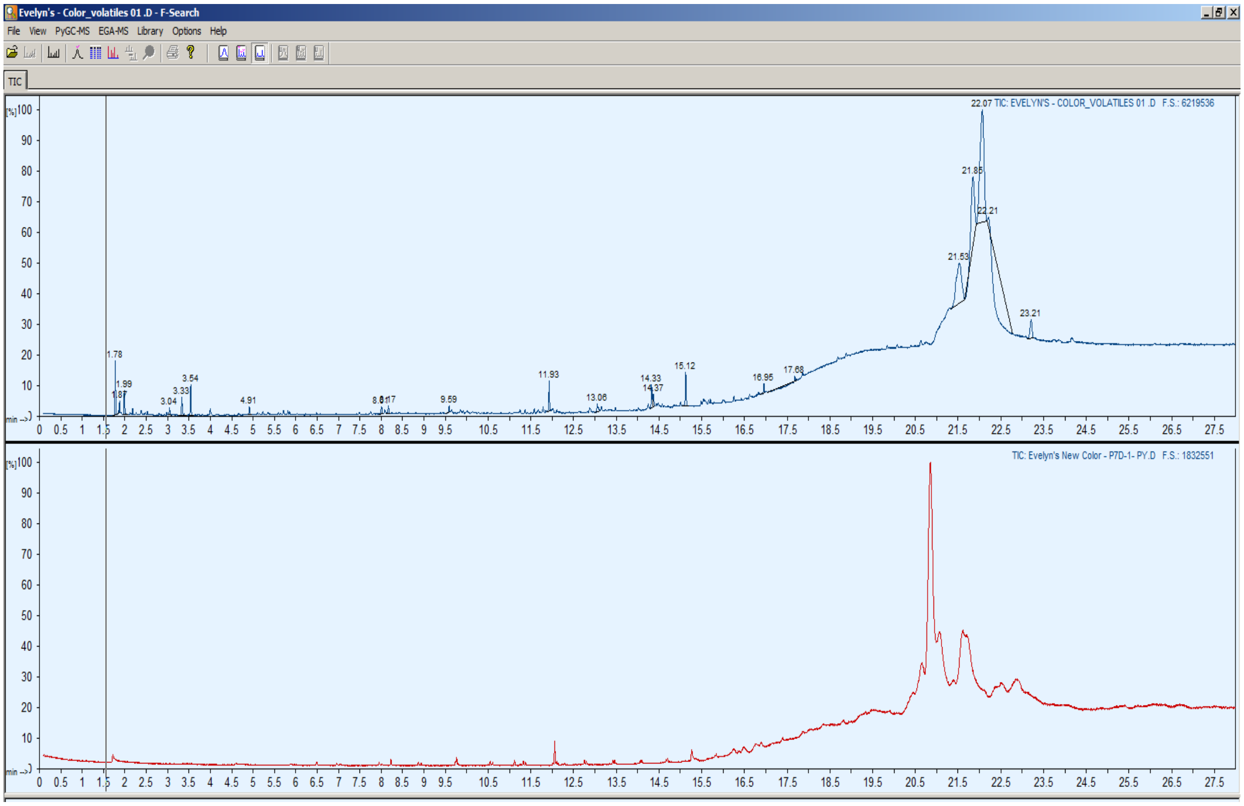


Figure C.6 Side by side comparison of both color additives

APPENDIX D

ANALYSIS OF COMPOUNDING INGREDIENTS

Chromatographic Analysis of Distearyl thio dipropionate (DSTDP)

Figures D.1 and D.2 show the results of the EGA thermogram and double shot chromatograms for DSTDP respectively

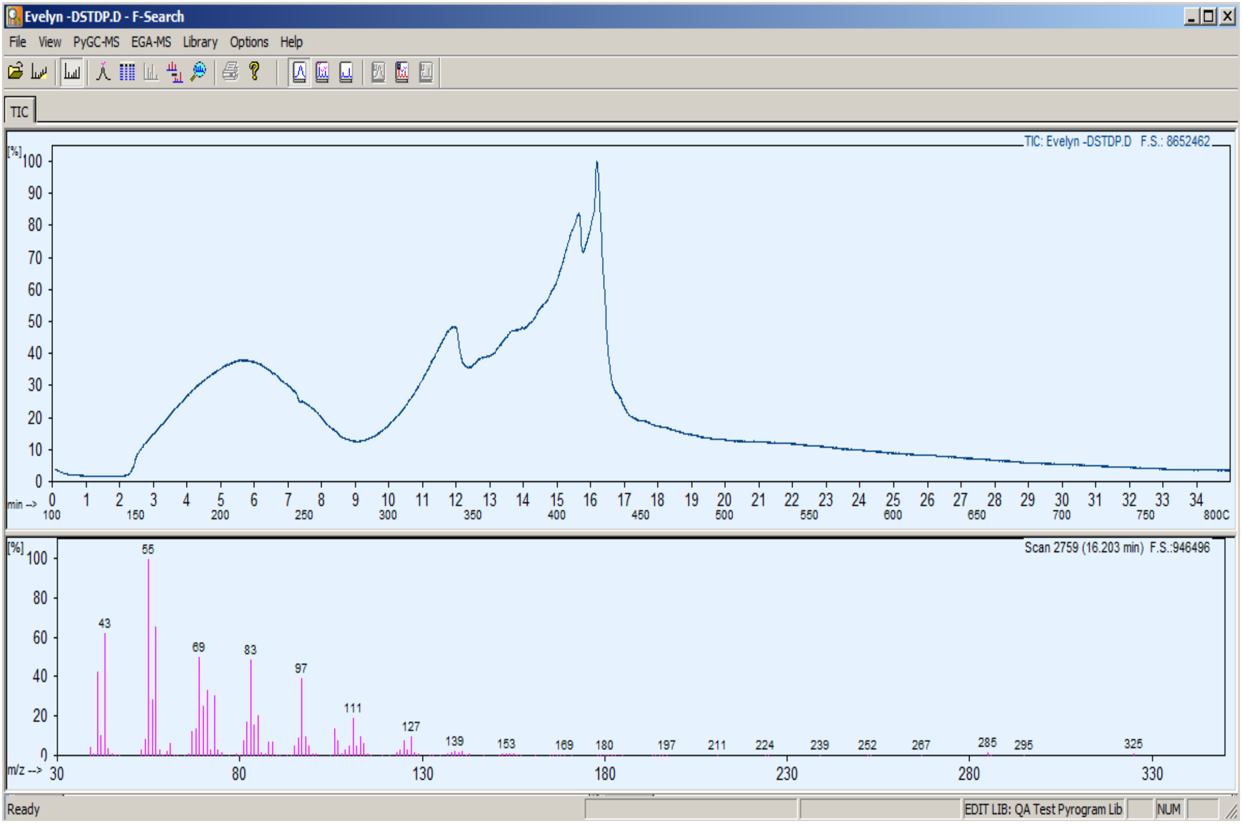


Figure D.1 Thermogram of EGA analysis for DSTDP.

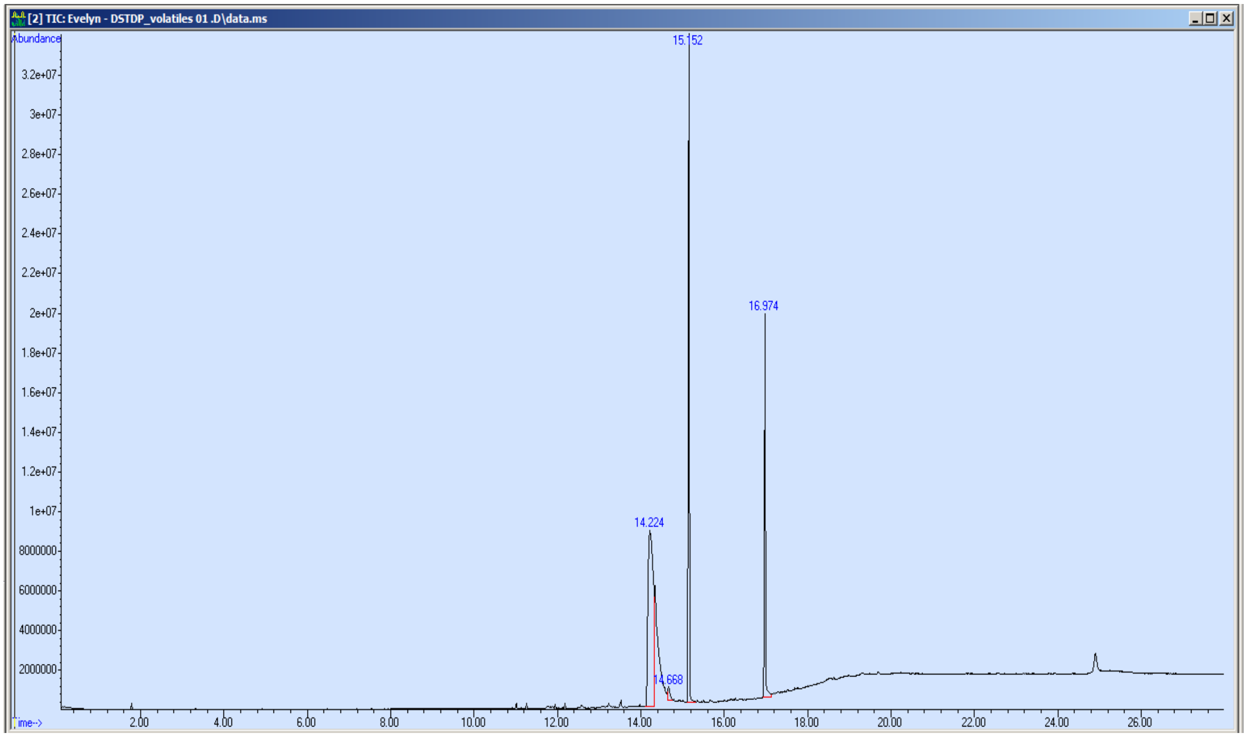


Figure D.2 Total ion chromatogram for the thermodesorption portion of DSTDP.

Table D.1 gives the list of compounds found to be present in the NIST and F-search libraries.

Table D.1 NIST and F-Search results for DSTDP

Table D.1	GC/MS NIST LIBRARY SEARCH RESULTS FOR DSTDP			F- SEARCH LIBRARY RESULTS FOR DSTDP			
Peak No.	Retention Time (mins)	Library/ID	Quality Match	Peak No.	Retention Time (mins)	Library/ID	Quality Match
1	14.224	1-Octadecene	99%	1	14.224	1-Octadecene	97%
2	14.668	Phenol, 4,4 ' -(1-methylethlyidene) bis	98%	2	14.341	1- Heneicosene	95%
3	15.152	Carbonic acid, octadecyl 2,2,2 - trichloroethyl ester	89%	3	16.974	Octadecyl 3 -mercaptopropionate	95%
				4	15.152	Acrylic acid tetradecyl ester	99%

Chromatographic Analysis of Epoxy

Figures D.3 and D.4 show the respective results of the EGA thermogram and double shot chromatograms of epoxy.

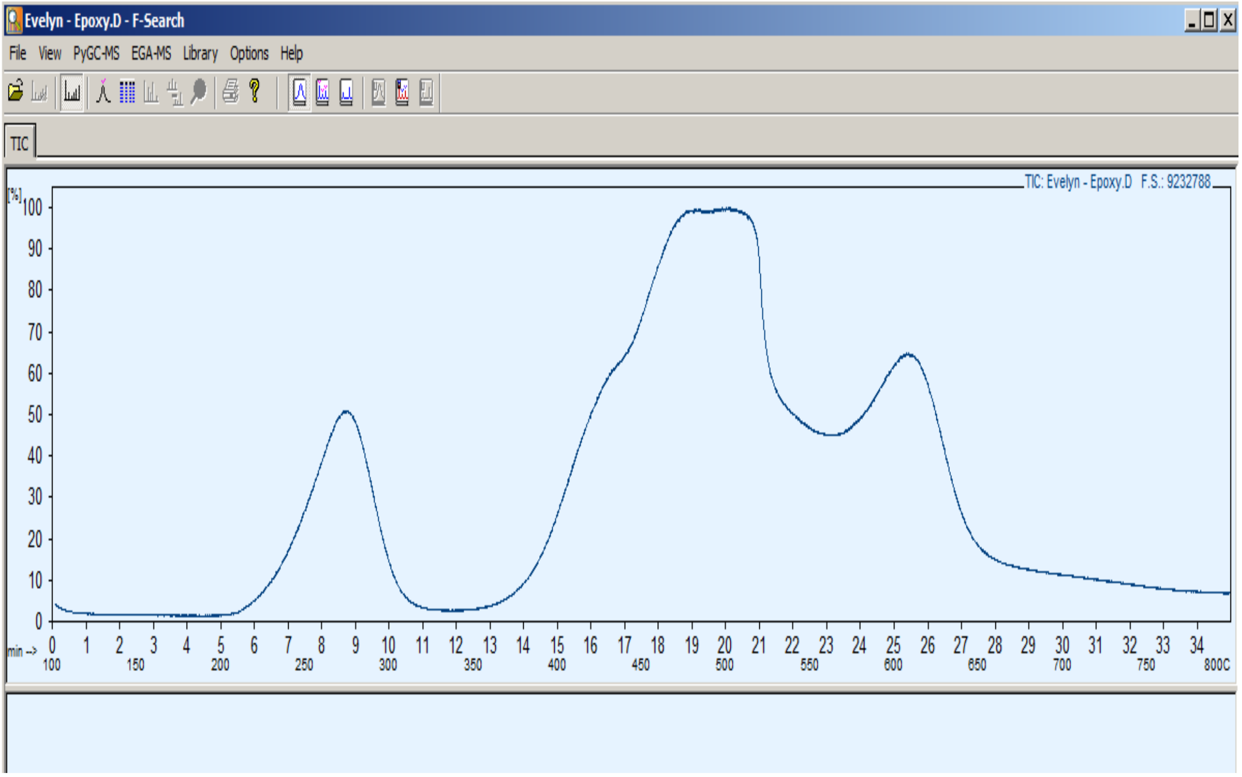


Figure D.3 EGA thermogram of epoxy.

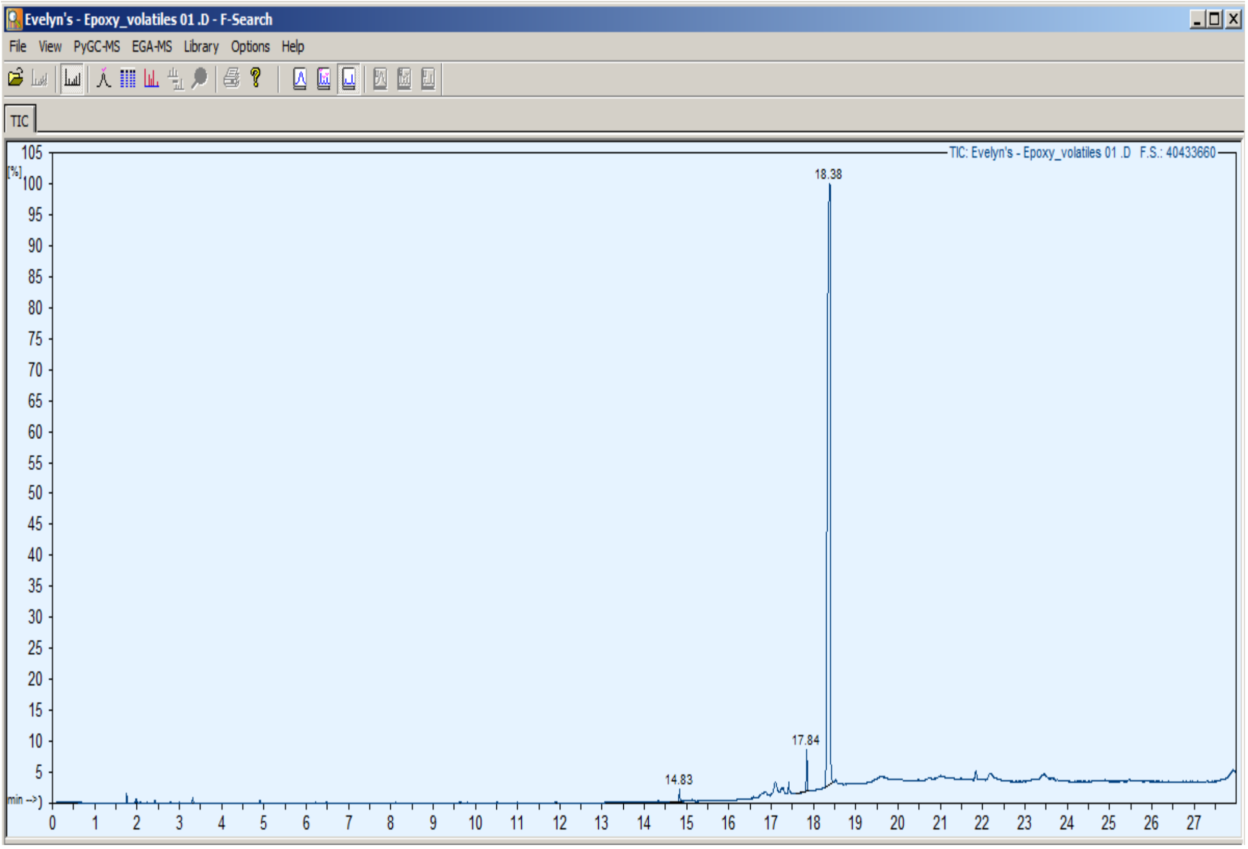


Figure D.4 Chromatogram of the thermal desorption portion for epoxy.

Table D.2 gives the list of the compounds that might be present using NIST and F-search libraries based on procedures 1 to 8 in appendix B.

Table D.2 NIST and F-Search results for Epoxy

Table D.2	GC/MS NIST LIBRARY SEARCH RESULTS FOR EPOXY			F- SEARCH LIBRARY RESULTS FOR EPOXY			
Peak No.	Retention Time (Mins)	Compound	Quality Match	Peak No.	Retention Time	Compound	Quality Match
1	14.831	Phosphine oxide, butyldiphenyl-	78%	1	17.838	2,2 (1-methylethyl diene) bis (4,1, phenyenoxymethylene) bis oxirane	93%
2	17.838	2,2 (1-methylethyl diene) bis (4,1, phenyenoxymethylene) bis oxirane	93%				

Chromatographic Analysis of Lubricant

Figures D.5 and D.6 show the respective results of the EGA thermogram and double shot chromatograms of lubricant.

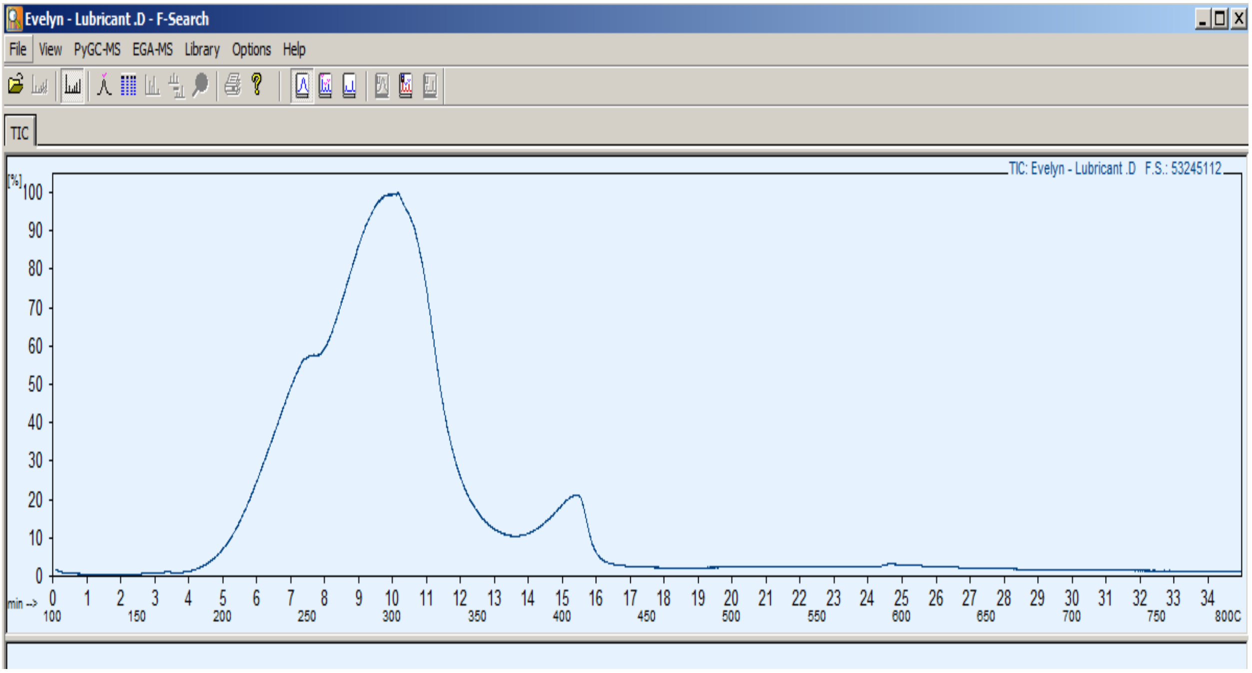


Figure D.5 EGA thermogram of lubricant.

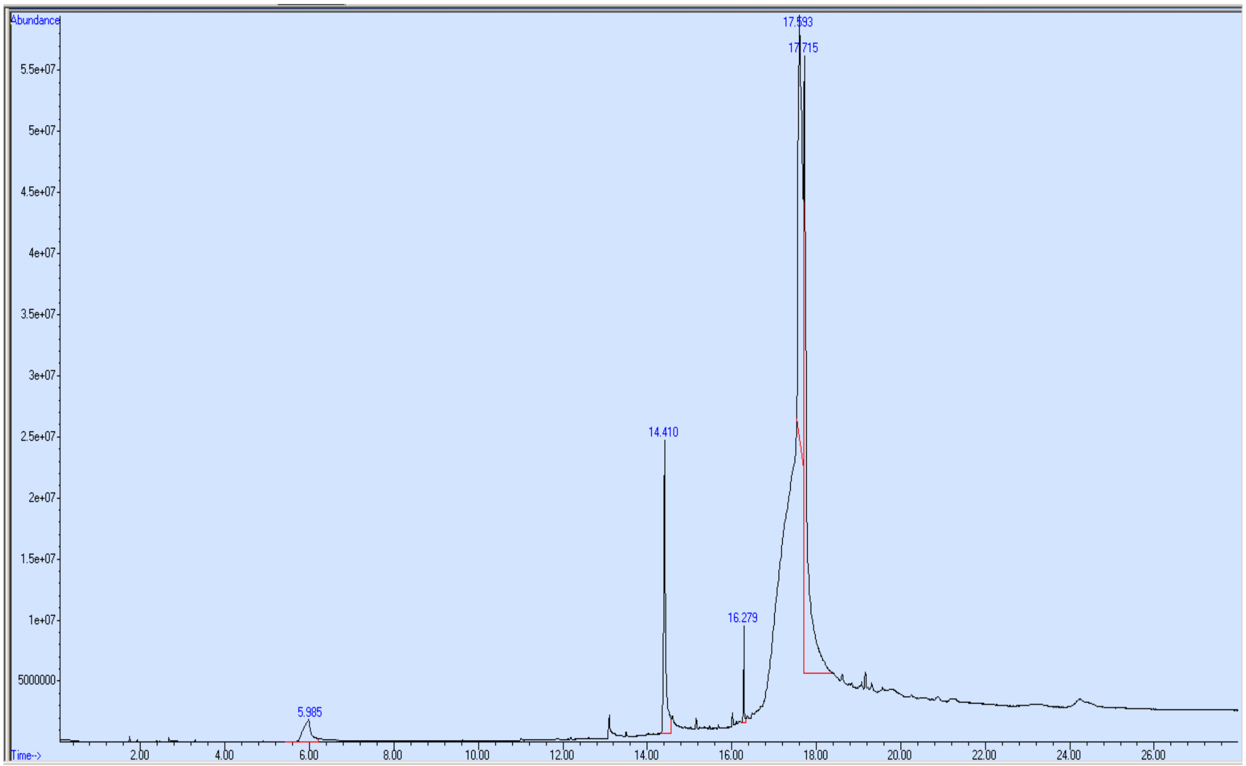


Figure D.6 Chromatogram of the thermal desorption portion for lubricant.

Table D.3 gives the list of compounds that might be present using NIST and F-search libraries based on procedures 1 to 8 outlined in appendix B.

Table D.3 NIST and F-Search results for lubricant

Table D.3	GC/MS NIST LIBRARY SEARCH RESULTS FOR LUBRICANT			F- SEARCH LIBRARY RESULTS FOR LUBRICANT			
Peak No.	Retention Time (Mins)	Library/ID	Quality Match	Peak No.	Retention Time	Library/ID	Quality Match
1	13.097	n-Hexadecanoic acid	99%	1	5.955	Glycerin	93%
2	14.410	Octadecanoic acid	99%	2	13.097	Palmitic acid	96%
				3	14.41	Stearic acid	94%
				4	17.593	Stearic acid monoglyceride	97%
				5	17.715	Stearic acid monoglyceride	92%

APPENDIX E

ANALYSIS OF THE REVISED FORMULATIONS IN PELLETS

Figures E.1 and E.2 show the chromatograms comparing the three formulations in pellets.

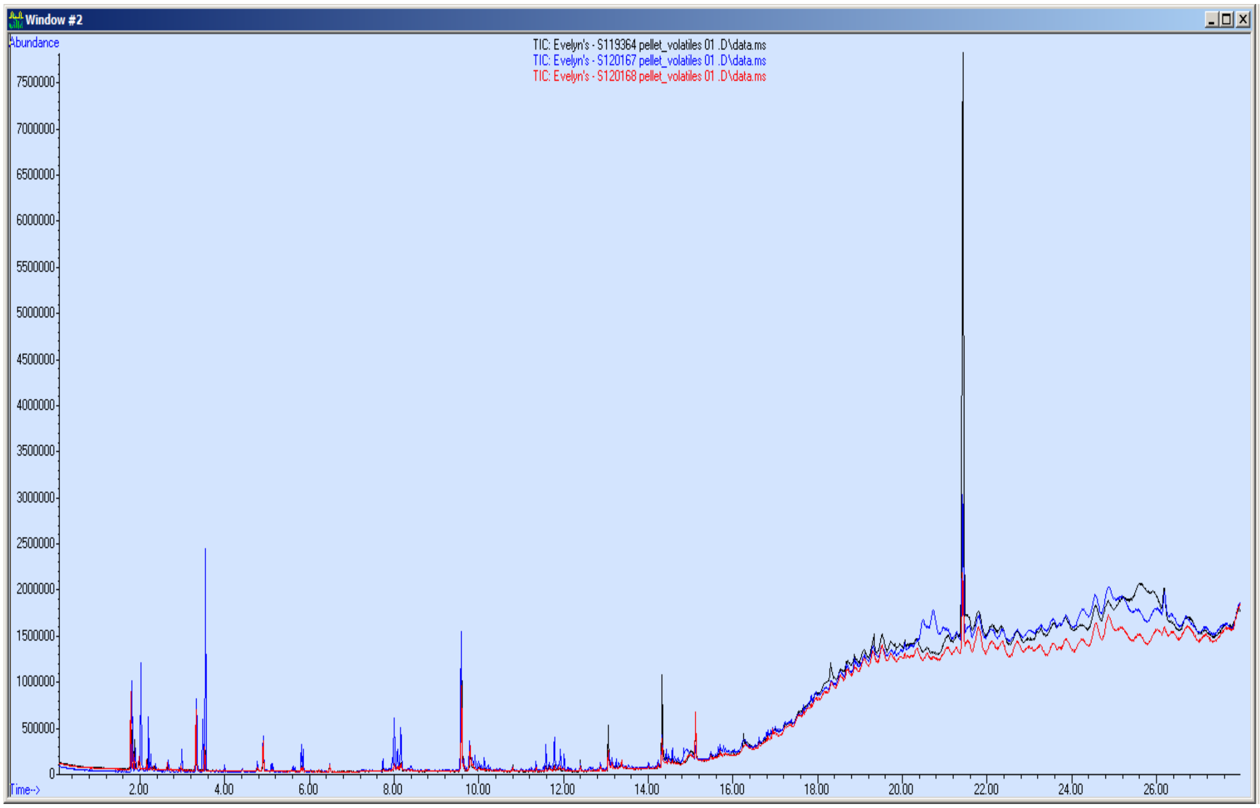


Figure E.1 Merged form chromatograms comparing the three formulations in pellets.

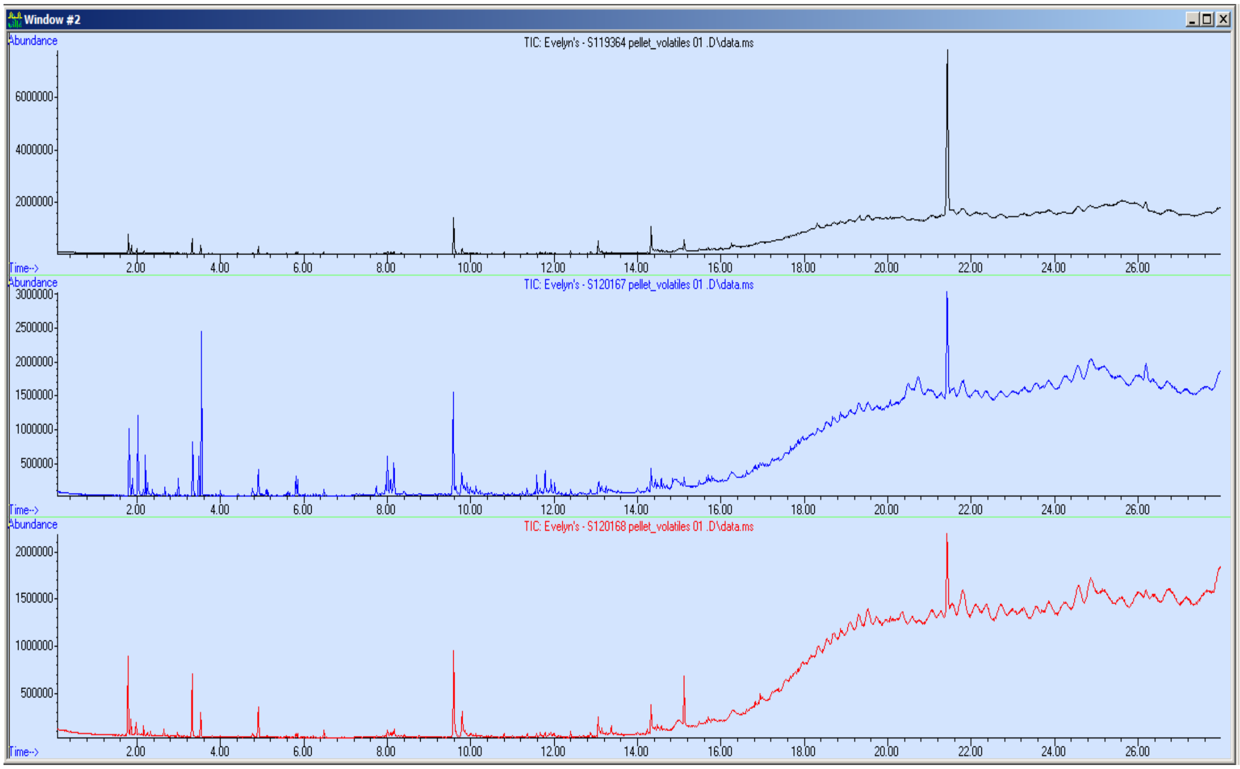
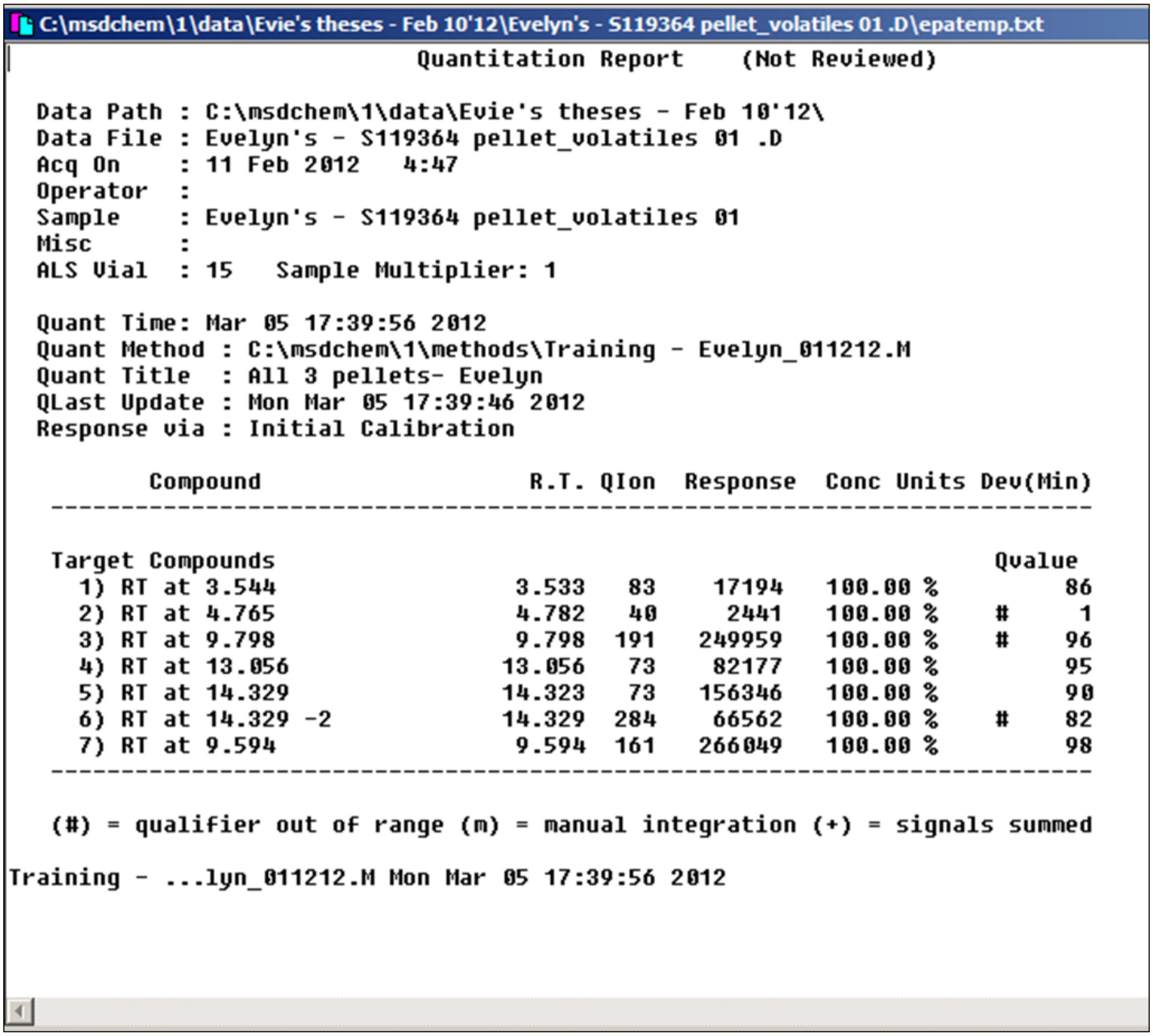


Figure E.2 Separate chromatograms comparing the three formulations in pellets.

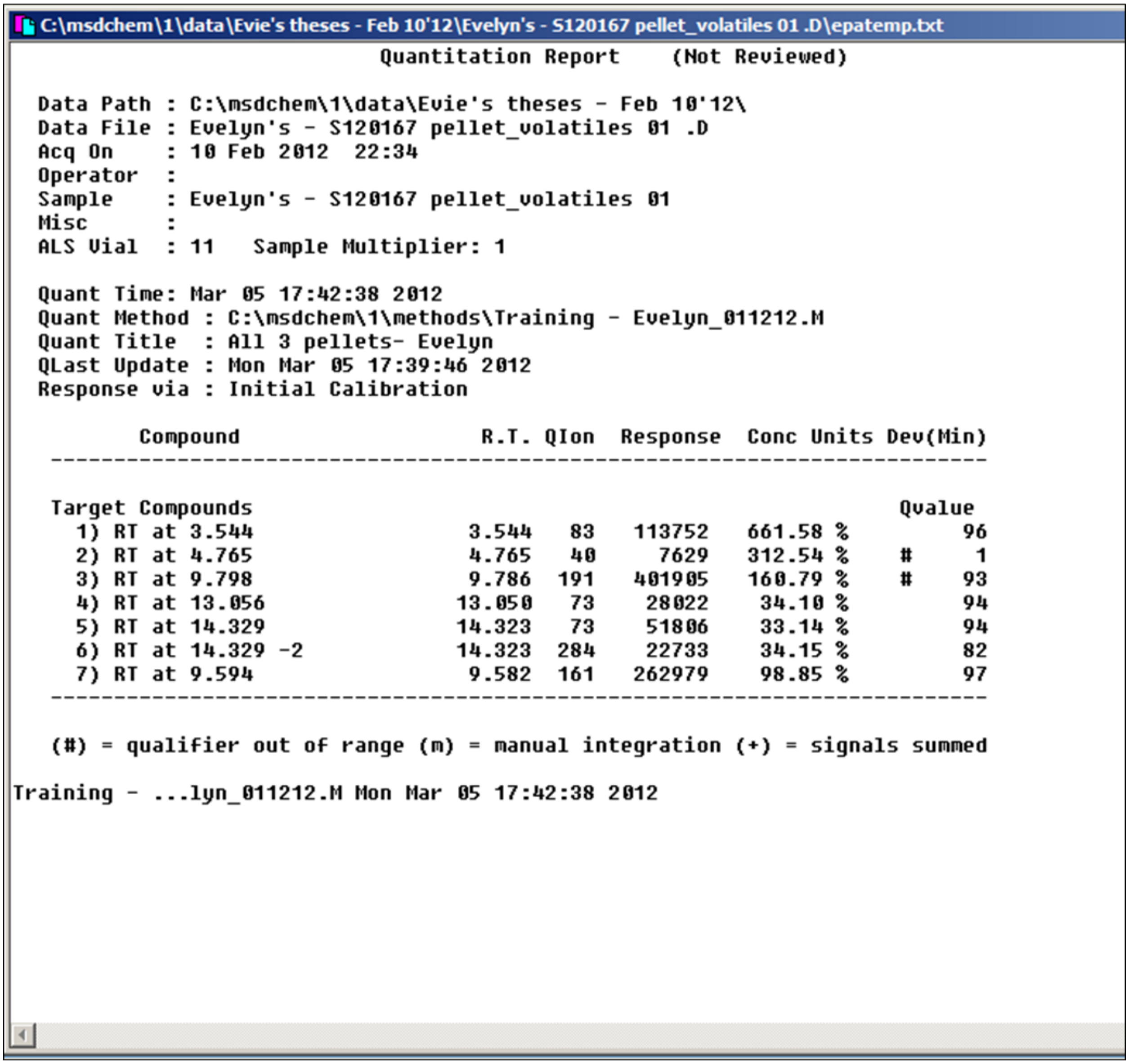
From Figures E.1 and E.2 the presence of some common peaks is seen although some have a higher peak area compared to others. Higher peak areas reflect a higher concentration of the compound. Since S119346 had the worst smell, it served as the control for the quantitation at concentration of 100%.

Figure E.3 shows the results of this quantitation for S119346. Figure E.4 shows the results of this quantitation for S112067. Figure E.5 shows the results of this quantitation for S112068.



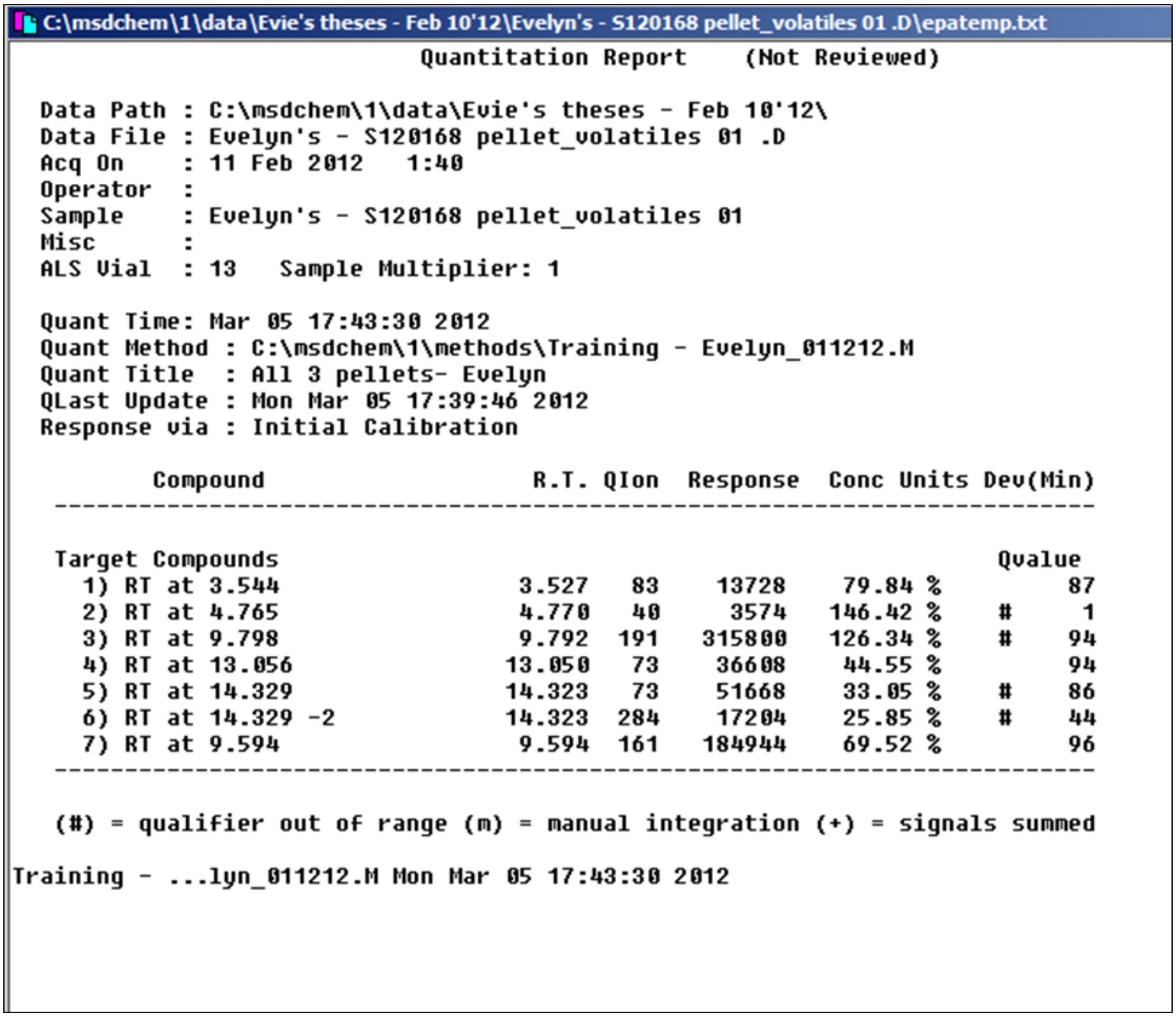
```
                              Quantitation Report    (Not Reviewed)

  Data Path : C:\msdchem\1\data\Evie's theses - Feb 10'12\
  Data File : Evelyn's - S119364 pellet_volatiles 01 .D
  Acq On    : 11 Feb 2012   4:47
  Operator  :
  Sample    : Evelyn's - S119364 pellet_volatiles 01
  Misc      :
  ALS Vial  : 15   Sample Multiplier: 1

  Quant Time: Mar 05 17:39:56 2012
  Quant Method : C:\msdchem\1\methods\Training - Evelyn_011212.M
  Quant Title  : All 3 pellets- Evelyn
  QLast Update : Mon Mar 05 17:39:46 2012
  Response via : Initial Calibration

          Compound                   R.T. QIon  Response  Conc Units Dev(Min)
   --------------------------------------------------------------------------

   Target Compounds                                                   Qvalue
     1) RT at 3.544                 3.533   83     17194   100.00 %        86
     2) RT at 4.765                 4.782   40      2441   100.00 %    #    1
     3) RT at 9.798                 9.798  191    249959   100.00 %    #   96
     4) RT at 13.056               13.056   73     82177   100.00 %        95
     5) RT at 14.329               14.323   73    156346   100.00 %        90
     6) RT at 14.329 -2            14.329  284     66562   100.00 %    #   82
     7) RT at 9.594                 9.594  161    266049   100.00 %        98
   --------------------------------------------------------------------------

   (#) = qualifier out of range (m) = manual integration (+) = signals summed

Training - ...lyn_011212.M Mon Mar 05 17:39:56 2012
```

Figure E.3 Compound quantitation for S119346 in pellets.



```
                              Quantitation Report    (Not Reviewed)

  Data Path : C:\msdchem\1\data\Evie's theses - Feb 10'12\
  Data File : Evelyn's - S120167 pellet_volatiles 01 .D
  Acq On    : 10 Feb 2012  22:34
  Operator  :
  Sample    : Evelyn's - S120167 pellet_volatiles 01
  Misc      :
  ALS Vial  : 11   Sample Multiplier: 1

  Quant Time: Mar 05 17:42:38 2012
  Quant Method : C:\msdchem\1\methods\Training - Evelyn_011212.M
  Quant Title  : All 3 pellets- Evelyn
  QLast Update : Mon Mar 05 17:39:46 2012
  Response via : Initial Calibration

          Compound                    R.T. QIon  Response  Conc Units Dev(Min)
   ---------------------------------------------------------------------------

   Target Compounds                                                   Qvalue
     1) RT at 3.544                  3.544   83   113752   661.58 %        96
     2) RT at 4.765                  4.765   40     7629   312.54 %    #    1
     3) RT at 9.798                  9.786  191   401905   160.79 %    #   93
     4) RT at 13.056                13.050   73    28022    34.10 %        94
     5) RT at 14.329                14.323   73    51806    33.14 %        94
     6) RT at 14.329 -2             14.323  284    22733    34.15 %        82
     7) RT at 9.594                  9.582  161   262979    98.85 %        97
   ---------------------------------------------------------------------------

   (#) = qualifier out of range (m) = manual integration (+) = signals summed

Training - ...lyn_011212.M Mon Mar 05 17:42:38 2012
```

Figure E.4 Compound quantitation for S120167 in pellets.



```
                             Quantitation Report    (Not Reviewed)

  Data Path : C:\msdchem\1\data\Evie's theses - Feb 10'12\
  Data File : Evelyn's - S120168 pellet_volatiles 01 .D
  Acq On    : 11 Feb 2012   1:40
  Operator  :
  Sample    : Evelyn's - S120168 pellet_volatiles 01
  Misc      :
  ALS Vial  : 13   Sample Multiplier: 1

  Quant Time: Mar 05 17:43:30 2012
  Quant Method : C:\msdchem\1\methods\Training - Evelyn_011212.M
  Quant Title  : All 3 pellets- Evelyn
  QLast Update : Mon Mar 05 17:39:46 2012
  Response via : Initial Calibration

        Compound                   R.T. QIon  Response  Conc Units Dev(Min)
   --------------------------------------------------------------------------

   Target Compounds                                                 Qvalue
     1) RT at 3.544               3.527   83    13728    79.84 %        87
     2) RT at 4.765               4.770   40     3574   146.42 %    #    1
     3) RT at 9.798               9.792  191   315800   126.34 %    #   94
     4) RT at 13.056             13.050   73    36608    44.55 %        94
     5) RT at 14.329             14.323   73    51668    33.05 %    #   86
     6) RT at 14.329 -2          14.323  284    17204    25.85 %    #   44
     7) RT at 9.594               9.594  161   184944    69.52 %        96
   --------------------------------------------------------------------------

   (#) = qualifier out of range (m) = manual integration (+) = signals summed

Training - ...lyn_011212.M Mon Mar 05 17:43:30 2012
```

Figure E.5 Compound quantitation for S120168 in pellets.

APPENDIX F

COMPARING PELLETS AND PLAQUES FOR FORMULATION S1120168

Figures F.1 and F.2 show the chromatograms comparing S120168 in pellet and plaque.

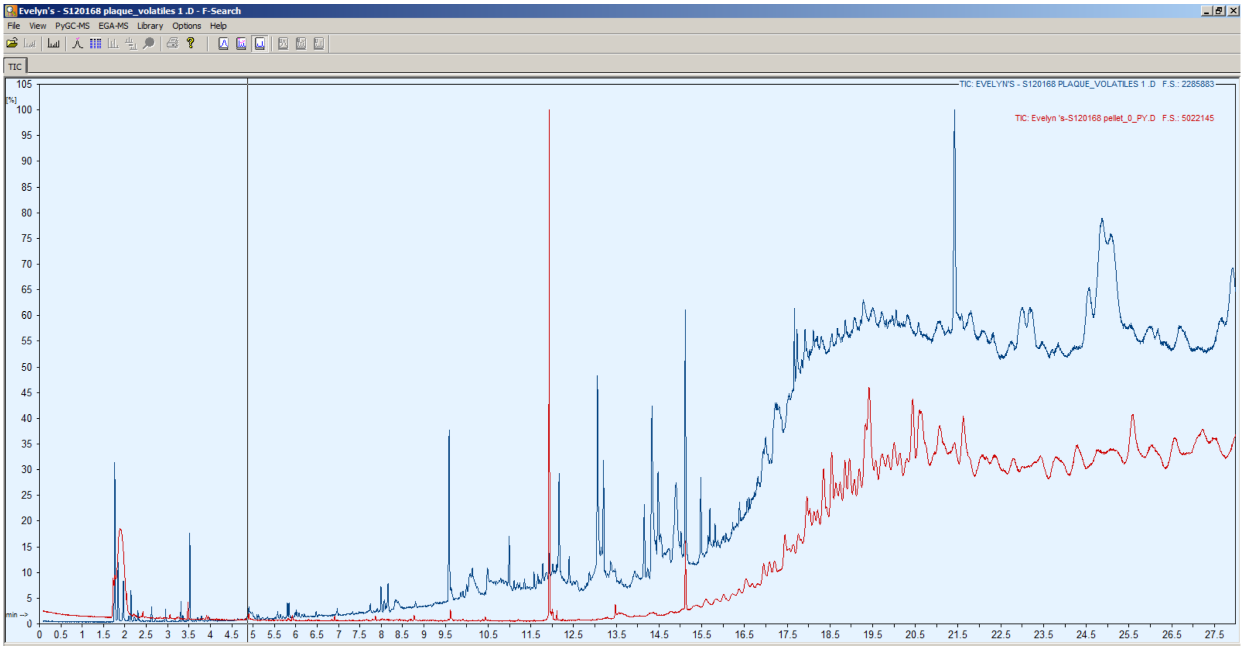


Figure F.1 Merged chromatogram comparing S120168 in pellet and plaque.

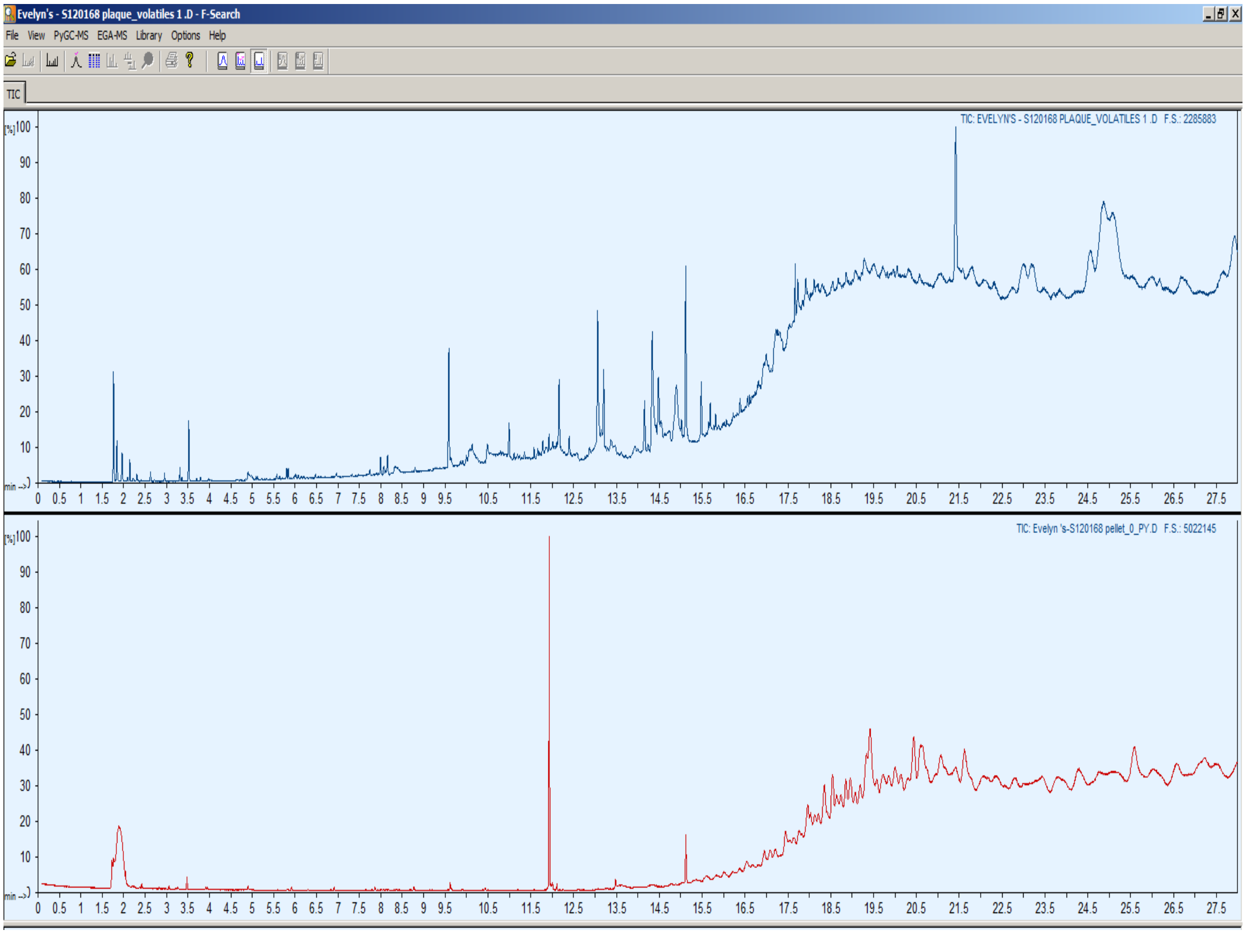


Figure F.2 Side by side comparison of pellets and plaques for formulation S120168.

APPENDIX G

COMPLETE LIST OF COMPOUNDS FOUND IN ANALYSIS

Table G.1 gives a compiled list of all the possible compounds present from GC/MS analysis.

Table G.1 Compiled list of all possible compounds present from our analysis using the GC/MS

List of possible compounds present in analysis			
Table G.1	Compounds	Table F.1 Cont.	Compounds
1	2-H Pyran, 3,4 - dihydro - 6 - methyl-	13	Acrylic acid tetradecyl ester
2	2,4 - Dimethyl - 1- heptene	14	2,2 (1-methylethyl diene) bis (4,1, phenyenoxymethylene) bis oxirane
3	1- Octadecene	15	Stearic acid monoglyceride
4	5 - Octadecen, (E) -	16	Glycerin
5	Eicosane	17	BHT -quinone-methide / Butylated Hydroxytoluene
6	Octadecanoic acid / stearic acid	18	Phenol, 2,4, - bis (1,1 -dimethylethyl)
7	n-Hexadecanoic acid / Palmitic acid	19	Tris (2,4-di-ter-butylphenyl)phosphite
8	Pyrene	20	Phosphine oxide, butyldipheyl-
9	Distearyl-3,3'-thiodipropionate	21	2 - methyl -1 - Pentene
10	1- Heneicosene	22	Phenol
11	Phenol, 4,4 ' -(1-methylethlyidene) bis	23	1- Pentene, 24,4, - trimethyl -
12	Octadecyl 3 -mercaptopropionate	24	Acrylic acid tetradecyl ester

- Carboxylic acids: Low molecular weight carboxylic acids can undergo oxidation which can result in strong malodors. Examples: stearic and palmitic acid.
- Thiols and –Mercapto: Sulfur containing compounds producing bad odor. Examples: distearyl-3, 3’-thiodipropionate and distearyl-3, 3’-thiodipropionate.
- Esters: Sweet smelling. Examples: acrylic acid tetradecyl ester.

- Phenols: Pungent smell. Examples: phenol and 1-methylethlyidene - 4, 4 – bis phenol.

APPENDIX H

GENERALIZED PROCESS FOR RESOLVING ODOR ISSUES IN MOLDED POLYMERS

The following steps outline the generalized procedure for resolving odor issues in molded polymers.

1. Observe the compounding process and identify if some process parameters can be optimized.
2. Obtain individual ingredients used in compounding polymer and evaluate each independently.
3. Identify offending ingredients using a smell test and use gas chromatography to identify compounds in those ingredients that may be contributing to odor. In performing the smell test, perform a blind test. This will prevent bias on the part of the participants.
4. Investigate the significance of each ingredient used in the process and choose alternatives that can be used as substitutes without altering the physical, mechanical and chemical properties of the final polymer.
5. If more than one ingredient could be contributing to smell, use several iterations to obtain the best formulation.
6. Since the molding process adds a different dimension to the final outcome of the molded polymer the different iterations in step 5 should all be subjected to the final molding process.
7. If odor is just a part of a complete test specification, perform the complete test to ensure that the improved polymer passes the complete test specification and not just odor.
8. Decide on which improved formulation to use based on data which shows the best most consistent values in the improved formulations.

VITA

Evelyn Lofquist was born in Accra, Ghana. She attended Kwame Nkrumah University of Science and Technology in Kumasi, Ghana after completion of her secondary school work at St. Mary’s Secondary School, Accra Ghana in 1998. She graduated with her Bachelor of Science degree from Kwame Nkrumah University of Science and Technology in June 2004. She immigrated into the U.S.A and has worked in various fields that included product development in the food processing and automotive industries respectively. She also worked in healthcare. During the winter, spring and summer semesters of 2009 and 2010 she attended The University of Michigan in Ann Arbor, Michigan. In August 2010, she entered the Graduate School at the University of Tennessee at Chattanooga. Evelyn accepted an opportunity graduate assistantship in the Student Support Services Division of the University of Tennessee at Chattanooga where she mentored and tutored minority and underrepresented students in STEM courses. This thesis was typed by the author.