

NOVEL ADHESIVES AND COATINGS FOR FOOD PACKAGING WITH LOW EXTRACTABLES

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ABSTRACT

Coatings made using monomer free technology have potentially lower levels of substances that can migrate through packaging materials. Extraction studies showed that UV cured coatings made with specific photoinitiators can have lower levels of extractables compared to analogous coatings cured with electron beam. Depending on coating chemistry, electron beam curing could result in side reactions that generate substances that have a tendency to migrate through packaging materials.

INTRODUCTION

There is tremendous potential for the use of radiation curable adhesives and coatings for use in packaging applications. One of the areas where there are significant opportunities is wide web offset and flexo for folding cartons. There is also potential for overprint applications on both porous and non-porous substrates. Laminating adhesives for multiwall bag packaging is another growth opportunity. In some cases, laminated structures may be replaced with radiation curable topcoats. All of these areas have been projected to receive significant growth over the next few years.

For successful growth of radiation curable coatings and adhesives in food packaging applications, inks, coatings and adhesives with no odor and very low levels of extractable substances are needed. Although UV curable systems have received most of the attention in the past, they had limitations that prohibited their use for most food packaging applications. In particular, residual unreacted monomers and photoinitiator fragments created undesirable odors and would migrate into food. There are two mechanisms whereby these substances can migrate into food. One mechanism was through volatilization and permeation through the packaging layers into food. The second mechanism occurs by diffusion from the UV cured side of packaging materials when sheets of packaging are stacked for storage with the UV cured side in contact with the food content surface.

In the past, the cost of electron beam curing equipment was very high. This limited the use of EB cured coatings and adhesives in many applications. Since the cost of EB curing units has decreased significantly in recent years, there has been an increased interest in the use of EB curable coatings and adhesives in packaging. It is commonly believed that EB curing has the potential of providing coatings and adhesives with lower odor and extractables.

It would be very significant if there were FDA approval for direct food contact of UV and EB cured coatings. Nevertheless, these materials are not restricted from use in food packaging applications provided that the current regulations are satisfied. The FDA regulations for food packaging materials relates to "food additives". Substances used in adhesives and coatings

are not considered to be food additives if they are not reasonably expected to become a component of the food. Exceptions to this are substances that are considered GRAS or are the subject of a sanction or approval issued by the FDA or USDA prior to enactment of the Food Additives Amendment of 1958. In addition, the substance can comply with an existing food additive regulation such as 21 CFR-176.170.

Many common components that migrate from UV or EB curable coatings would not be in compliance as food additives. Therefore, it is important that these substances not become a component of food. One way is through the use of a suitable barrier that prevents them from migrating into food. Another method is through the development of UV and EB curable coatings and adhesives that do not have unapproved substances that have a tendency to migrate into food. In this case suitable extraction studies simulating the intended conditions of use are necessary to prove that there are not any unregulated substances migrating into food that would then be classified as a food additive. According to the FDA, substances that migrate into food must not be greater than 50 parts per billion in the food.

In this paper, we describe unique monomer free UV cured coating technologies that have low extractables. By proper choice of matrix oligomers, photoinitiators and compounding ingredients, we have been able to produce UV cured coatings that have potentially lower extractables than comparable EB cured coatings.

EXPERIMENTAL

The coating compositions used for extraction testing were based on our proprietary monomer free UV coating technology. These coatings are low viscosity liquids and they are produced by conventional mixing conditions. These monomer free compositions are compared to a conventional monomer containing coating as well as analogous EB cured coatings that do not contain photoinitiator.

Coatings were coated on 1 mil aluminum foil using a hand proofer from Pamarco. This technique resulted in a consistent coating weight around 2 pounds/ream. The coatings were cured by passing them through a Mini conveyerized UV curing system manufactured by American Ultraviolet. This unit had a 300-watts/inch medium pressure mercury lamp equipped with a focused reflector. The line speed was 60 feet/minute. Radiation intensities were measured using an EIT Model UV Power Puck Radiometer. The curing conditions are listed in Table 1. Electron beam curing was carried out using laboratory equipment at Energy Sciences, Inc. The conditions for curing with electron beam were 3 mega rads and 1.75 KV.

TABLE 1
UV CONDITIONS USED FOR CURING COATINGS

UV WAVELENGTH REGION	JOULES/CM ² (DOSAGE)	WATTS/CM ² (INTENSITY)
UVA	0.120	0.391
UVB	0.106	0.340
UVC	0.015	0.046
UVV	0.063	0.200

The coated foil samples were tested for coating borne extractables using the Cell Extraction procedure and 10% ethanol as a food simulating solvent. Sections of each foil sample were cut and placed into a custom stainless steel extraction cell designed according to FDA specifications for food contact polymer migration testing. The extraction conditions were 24 hours at 40^o C with constant agitation. After extraction, ultra high purity distilled water was added to the ethanol solutions along with anthracene-*d*₁₀ internal standard and 5 mls of methylene chloride. The samples were vigorously back extracted and centrifuged. The methylene chloride layers were then transferred to conical-bottomed vials and concentrated to 0.1 ml using a nitrogen stream. The concentrated extracts were analyzed by GC-MS using optimum conditions for testing of extractable substances.

The concentrated extracts were injected into a Varian 3400 gas chromatograph equipped with a 30 meter MDN-5 column. The injector temperature was 260^o C and the column chamber was programmed to ramp from 50^o C to 320^o C at 10^o C/minute. The GC was interfaced with a Finnigan MAT 8230 mass spectrometer.

RESULTS AND DISCUSSION

Our focus has been to develop a family of low extractable radiation curable coatings for labels, folding cartons, food packaging and pharmaceutical applications that provide excellent graphics. For this, we have developed a proprietary resin technology that does not require the use of acrylate monomer diluents. These coatings that do not contain monomers result in improved worker safety, lower press side odor and reduced potential for skin irritation. In addition, the potential for migration of residual components of the coating to the packaged material is greatly reduced. Using the proprietary monomer free technology, it is possible to formulate coatings for a variety of applications that provide the same performance characteristics as monomer containing coatings. In Table 2, the performance properties of a monomer free coating are compared to that of a typical monomer containing coating. These coatings are both formulated as medium slide angle UV curable overprint varnishes. Since coating compositions that do not contain low molecular weight monomers should have less

migration tendencies, we evaluated several coatings with different compositions. These coatings were cured using the conditions described earlier. The coating compositions

**TABLE 2
COMPARISON OF COATING PROPERTIES**

PROPERTY	MONOMER BASED COATING	MONOMER FREE COATING
Viscosity, cps, 25 ^o C	160 - 200	320 – 400
Weight/gallon, 23 ^o C	9.3 lbs	9.3 lbs
Wet Color	Light Straw	Water White
Color After Cure	Clear, High Gloss	Clear, High Gloss
Recommended Coating Weight, lbs/3000 ft ²	1.8 – 2.2 lbs/3000 ft ²	1.8 – 2.2 lbs/3000 ft ²
Cure Conditions	100 Millijoules/cm ²	100 Millijoules/cm ²
60 ^o Gloss	80 +	80 +
Slide Angle	15 - 20	10 – 15
1000 Sutherland Rubs, 4# Weight	No Scuffing or Scratching	No Scuffing or Scratching

**TABLE 3
COATINGS EVALUATED FOR MIGRATION POTENTIAL**

SAMPLE	COMPOSITION	TYPE OF CURE
Coating A	Monomer Based Coating, Low MW Photoinitiator #1	Medium Pressure Mercury Lamp
Coating B	Monomer Free Coating, Low MW Photoinitiator #2	Medium Pressure Mercury Lamp
Coating C	Monomer Free Coating, Low MW Photoinitiator #3	Medium Pressure Mercury Lamp
Coating D	Monomer Free Coating, Polymeric Photoinitiator	Medium Pressure Mercury Lamp
Coating E	Monomer Free Coating, High Efficiency Photoinitiator	Medium Pressure Mercury Lamp
Coating F	Coating E With 1/5 Level of Photoinitiator	Medium Pressure Mercury Lamp
Coating G	Monomer Free Coating, No Photoinitiator	Electron Beam
Coating H	Monomer Free Coating, No Photoinitiator	Electron Beam

that were evaluated are summarized in Table 3. In these experiments, a comparison is made of monomer-based coatings to the monomer free technology using different photoinitiators.

In addition, monomer free coatings without photoinitiator were cured using electron beam. Extraction studies were carried out on aluminum foil that was coated with the various samples listed in Table 3. The data obtained from the extraction studies done on UV cured coatings are summarized in Table 4. The materials that were extracted are organized into different classes of compounds.

**TABLE 4
EXTRACTION OF UV CURED COATINGS**

Substance	# A, ppb	# B, ppb	# C, ppb	# D, ppb	# E, ppb	# F, ppb
Inhibitors, antioxidants	877	106	58	76	53	76
Photoinitiator Fragments	260	1126	23	282	8	6
Photoinitiator	11,467	3,083	1,438	540	573	32
Fatty Alcohols	3	1,222	115	271	153	711
Heterocyclic Hydrocarbons	20	44	8	12	6	
Acrylate Oligomers	1043		48	120		574
Miscellaneous Organics	68	130	5		95	194
Total Extractables	13,738	5,711	1,695	1,301	888	1593

As expected, Coating A which is a monomer containing system using a low molecular weight photoinitiator gave the highest level of extractable substances. All of the monomer free compositions (Coatings B – F) gave much lower levels of extractables. Coatings B – F were identical except for the level and type of photoinitiator. The results show that the type of photoinitiator has a significant effect on the amount of extractable unreacted photoinitiator, photoinitiator fragments and other by products. The lowest level of extractable substances was obtained with Coating E. This coating utilized a proprietary photoinitiator that was designed to work well with the monomer free coatings. This photoinitiator is more efficient resulting in less extractable unreacted photoinitiator and photoinitiator fragments. Coating F is the same as Coating E except that 1/5 of the level of the high efficiency photoinitiator was used. Although this coating appeared to cure well, there were significantly higher levels of extractable acrylate oligomers. This indicated that Coating E was more thoroughly cured than Coating F. However, it is interesting to note that there was a significantly lower level of extractable free photoinitiator in coating F. This suggests that further studies to optimize the level of photoinitiator could result in coatings that are significantly free of extractable substances.

Extraction studies were also performed on electron beam cured coatings. These compositions were made using the monomer free technology and without photoinitiators. It is interesting to note that these compositions (Coatings G, H) that were cured using electron beam had higher levels of extractables compared to Coating E. Although extraction of the

electron beam cured coatings did not result in any unreacted photoinitiator or photoinitiator fragments, there were higher levels of other substances. Electron beam curing is initiated by high-energy electrons. These electrons collide with electrons on the ingredients of the coating to generate free radicals. In the presence of unsaturated molecules, polymerization is initiated resulting in cure of the coating. Depending on the chemistry of the coating ingredients, the high-energy electrons could also remove electrons from various compounding ingredients used in the coating resulting in molecular fragments that later show up in extraction studies.

**TABLE 5
EXTRACTION OF ELECTRON BEAM CURED COATINGS**

Substance	# G, ppb	# H, ppb	# E, ppb
Inhibitors, Antioxidants	103	349	53
Photoinitiator Fragments			8
Photoinitiator			573
Fatty Alcohols	953	665	153
Heterocyclic Hydrocarbons	39	55	6
Acrylate Oligomers	31	69	
Miscellaneous Organics	97	111	95
Total Extractables	1223	1249	888

CONCLUSIONS

The results of this study demonstrate that it is possible to make UV cured coatings that have low levels of extractables through the use of monomer free technology and the proper choice of photoinitiator. UV cured coatings can be formulated to have levels of extractables that are equivalent or lower than electron beam cured systems. Further work to optimize the photoinitiator level in monomer free coatings should result in further reduction of extractable substances. For electron beam cured coatings, it is important to consider the chemistry of all of the compounding ingredients used in the coating since additional fragmentation reactions could occur resulting in low molecular weight fragments that would have a tendency to migrate into food. Each coating needs to be considered on an individual basis to determine whether it is potentially compliant with the FDA regulations.

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