



**HIGHLY STABILIZED
FLAME RETARDED
POLYOLEFIN INSULATION COMPOUNDS**



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ABSTRACT

Polyolefin compounds used in many residential and industrial wire insulations are often required to have a balance of properties in electrical, physical, processability, and flame retardancy to meet material specifications. In applications that demand high service temperatures and thermal stability, these compounds are further crosslinked either chemically or with irradiation, and stabilized with high levels of antioxidants.

Strategies to design flame retarded (FR) insulation materials with a specific target for a 150°C rated appliance wire insulation is the subject of this paper. Approaches to use different technologies in FR, antioxidants (AO), and crosslinking to achieve a balance of properties are discussed as well as the effects of base resin, halogenated vs. non-halogenated FR additives, and copper catalyzed thermal degradation. Experimental design was used to optimize the compound's performance in oven aging and cure efficiency.

INTRODUCTION

Polyolefinic materials used to make cable insulation in low voltage (less than 1kV) applications such as power cables, control cables and appliance wire are required to have a multitude of properties compliant with the UL 44 standard and the various application-specific styles. Often times, end users demand even higher performance levels than those specified in the standards. Hence this class of compounds represents significant technical and development challenge to the material suppliers. A broad knowledge of flame retardant, antioxidant, base resin, filler and processing to achieve a balance of properties is critical in designing these compounds.

Recent advances in areas of flame retardant, antioxidant, and related technologies¹⁻⁴ signal there are opportunities to improve product performance and cost effectiveness. The current specifications for the 150° C rated appliance wire insulation require heat aging at 158°C for 150 days and VW-I flame resistance.

The intrinsic difficulty in achieving long term heat stability is the need to have a high level of antioxidant which causes problems in compatibility (blooming), chemical interference leading to poor cure and high cost. Another issue in thermal stability is the detrimental copper effect as a result of the insulation having direct contact with the conductor. Conventional metal deactivating antioxidants are effective only in lower temperature ranges and are limited to thermoplastic applications.

The need for high levels of antioxidants creates a difficulty in crosslinking. Hindered phenolics which are effective long term thermal stabilizers invariably interfere with peroxide crosslinking, and to a lesser extent, with irradiation crosslinking.⁵ Simple addition of more AO or peroxide does not necessarily improve their performance, but rather may diminish their effectiveness.

It is the intent of this paper to describe work to design crosslinkable FR insulation compounds with high thermal stability. Experimental results in studying the effects of base resin, FR additives, and copper-catalyzed degradation in oven aging are presented. These results were used in the design of a 150° C compound. Experimental design was employed in the study to optimize heat aging and cure and its performance was compared to a commercial product.

EXPERIMENTAL

SAMPLE PREPARATION

Heat age samples were made by blending the components in a 240 cc Brabender for 8 min. at a melt temperature applicable to the base resin. All additives were commercial grade and used without further purification. The resulting mixture was prepared according to ASTM D 638 method for tensile and elongation testing. The samples were compression-cured for 20 min at 375°F. The specimens were aged in a convection oven at the preset temperature. The test for brittleness was determined by bending and pulling the specimen several times. The specimen fails if any crack appears. Three replicates were used for each sample.

WIRE COATING

Wire samples were made on a 3.5 " diameter extruder with a 20/1 L/D. The temperature profile was set at 220-235°F on the various zones. The wire construction consisted of #18 16/30 tin coated copper conductor with 30 mil wall thickness.

EXPERIMENTAL DESIGN PROGRAM

Experimental design, model fitting and analyses were done with JMP version 3.1 from SAS Institute Inc. on an IBM PS/2E computer. The Box-Behnken table was generated from the response surface design selection. Model fitting was done in the response surface/effects screening mode. The resulting parameters were analyzed. Higher order terms (other than the liner coefficients) that contained probability t values greater than 0.01 were deleted and the fitting step was repeated. This iteration process continued until the remaining terms had t values < 0.001.

RESULTS AND DISCUSSION

SCREENING OF AO SYSTEMS AND COPPER EFFECTS IN ACCELERATED HEAT AGING

Long term thermal stability of polyolefin compounds is inherently difficult to assess due to the length of testing period. The accepted requirement for the 150°C rated appliance wire is >50% retention of elongation after 150 days at 158°C. To reduce the test duration an accelerated test at 180°C for 21 days was chosen to evaluate several primary AO systems. There are concerns in the validity of accelerated testing, however. It is recognized that there are controversies in applying the Arrhenius law in heat aging.⁶ Physical processes such as deformation, molecular diffusion, and annealing all contribute to the overall temperature dependence in addition to chemical degradation. These factors, however, are less significant in crosslinked filled polymers where chain mobility is severely limited.

After screening nearly thirty different AO formulations covering the general classes of stabilizers used in polyolefins, three systems were selected for further study. They were A01, a package currently used in a commercial XL polyethylene compound which consists of a hindered phenol and a thioester; A02, a system consisting of a hindered phenol and a sulfur-containing additive and A03, a proprietary system developed internally which contains no phenolics. The AO's were tested at normal levels and high levels in two types of ethylene-copolymers which were selected for filler/additive compatibility. The copolymers chosen were ethylene-n-butyl acrylate (EnBA) and ethylene-vinyl acetate (EVA) at comparable monomer content (18% w/w). Copper powder was added at 100 ppm for evaluating copper-catalyzed degradation. Plaque samples containing 1.3% Vulcupr were cured and heat aged at 180°C until cracking or brittleness was observed. The results are given in Table I.

TABLE I: SCREENING OF AO SYSTEMS (Days to Brittleness)

AO SYSTEMS	XL-EVA	XL-EnBA		
	No Cu	100 ppm Cu	No CU	100 ppm CU
A01	10	7	11	6
A02	9	7	13	10
A02 *(High Level)	15	11	14	10
A03	11	8	12	9
A03 (High Level)	21	11	17	10

As seen, both commercial AO systems failed to reach 21 days even in the absence of copper. The new AO package at high level reached 21 days without copper but fell to 11 days with copper. The copper effect is significant, as polymer integrity was decreased 20-50%.

The mechanism of copper catalyzed autooxidation of polymers is well-documented.⁷ It is believed that copper ions (I and II) accelerate the decomposition of polymer hydroperoxides to chain degrading radical species. Utilization of chelate chemistry to immobilize copper ions has been used to develop deactivators. The copper deactivator currently used in telecommunication insulation, Irganox 1024 is very effective because of its hydrazine functional group in addition to the hindered phenolic groups. However, its commercial success is largely limited to thermoplastics where aging temperatures seldom go above 120°C. To determine whether Irganox 1024 is useful at higher temperatures, it was added to AOI in EVA and aged at 165 and 180°C. In this experiment, passing was >50% elongation retention. The results are given in Table 2.

TABLE 2: EFFECTS OF Cu DEACTIVATOR

SAMPLE	AOI	IRGANOX 1024 (%)	Cu	165°C	180°C
1	Normal	None	200	Fail	Fail
2	Normal	0.1	200	Pass	Fail
3	High	0.1	200	Pass	Fail
4	Normal	0.1	None	Pass	Fail
5	High	0.1	None	Pass	Pass

Samples 1-3 are controls to show that 200 ppm Cu was sufficient to cause AOI to fail at the normal level (Sample 1). In the absence of Cu, adding 0.1 % Irganox 1024 to AOI at the normal level enabled the resin to pass at 165°C (but not at 180°C) and passed both temperatures at the higher AOI level. Samples 4 and 5 show that the metal deactivator is ineffective at 180°C.

FR AND BASE RESIN EFFECTS IN ACCELERATED HEAT AGING

The knowledge of how FR additives influence resin thermal stability (not combustion property) is largely empirically based. In theory, additives that produce reactive species that catalyze polymer degradation are detrimental to heat aging. Conversely, additives that scavenge harmful species help stabilize resins. Bromine FR additives are not known to have harmful effects in polyethylenes although corrosive bromine species may be produced at higher temperatures. Hydrated fillers such as aluminum trihydrate and magnesium hydroxide which have basic surfaces can neutralize acidic species. There are very few published studies⁸ on these effects, thus it was instructive to compare several FR packages their impact on heat aging. Four bromine-antimony oxide systems (11% total) and one non-halogenated additive (30%) were tested with AO3 and the results are given in Table 3.

TABLE 3: EFFECTS OF FR IN HEAT AGING

FR SYSTEMS	DAYS TO BRITTLINESS	Br TYPE
None	10	—
BR-FR 1	19	Aromatic Br, With O
BR-FR 2	17	Aromatic Br Only
BR-FR 3	15	Aromatic Br, With O
BR-FR 4	12	Aliphatic Br With O
Non-Hal	15	—

There is no systematic similarity in the bromine additives except that they are all commercially available. BR-1 contains aromatic Br, O, and N; BR-2 contains aromatic Br only; BR-3 contains aromatic Br and O; and BR-4 contains aliphatic Br and O. Oven aging at 180°C indicated that the FR additives improved stability substantially in the presence of copper. With BR-1 the extension of stability to 19 days was particularly encouraging.

The mechanism of the observed enhancement due to Br additive and whether this synergy exists in other AO systems remains unknown. The fact that BR-I contains both O and N and also gave the best improvement suggests that the additive itself or its impurities may have some copper complexation properties thereby counteracting some of the copper effects. Although not addressed in the current study, this apparent synergy would be an interesting area to investigate with more refined analytical techniques such as TGA. An understanding of the mechanism could lead to developing a more robust metal-deactivator that is useful in high temperature applications.

Copolymers such as ethylene-vinyl acetate and ethylene-ethyl acrylic acid are generally used to make highly filled compounds because of their good flexibility and additive compatibility. The disadvantages, however, are their lower thermal stability and electrical insulation due to the presence of large number of polar side chain. In this study we have investigated three resins for heat aging. They were EVA, EnBA, and EMA. AO3 and BR-I were added to each and aged at 180° C until brittleness. As seen in Table 4, EnBA yielded the best results while EMA gave the poorest.

TABLE 4: EFFECTS OF BASE RESIN IN HEAT AGING

RESIN	HEAT AGE
EVA	16
EnBA	17
EnBA	16
EMA	13

Several factors have to be considered in speculating the heat aging performance of the resins. First, copolymer stability is largely determined by the ease of breaking the side chain from the polymer backbone. Since EVA contains C-O bonds (60-65 kcal/mole) which are weaker than C-C bonds (70-75 kcal/mole) in EnBA and EMA, one would expect EVA to be the least stable. Another factor is diffusion of decomposed species within the polymer matrix to catalyze degradation, especially if they are acidic. It is speculated that EnBA would decompose to give n-butyric acid or butanol which diffuses slower than acetic acid or methanol as in EVA or EMA. Finally, crosslinking via ester groups in these polymers leading to loss of elongation (brittleness) could be significant, especially with EMA. It is very difficult to establish which of these factors is the main reason for EnBA's superior heat stability.

FLAME RETARDANCE AND PHYSICAL PROPERTIES OF INSULATION COMPOUNDS

The UL 44 standard specifies a VW-I FR rating for most of the low voltage appliance wires. To achieve this level of fire resistance requires substantial amount of flame retardants. Invariably the electrical insulative and physical properties of the resin suffer. Non-halogenated FR additives such as ATH and magnesium hydroxide have advanced in recent years mainly in coating technologies to improve polymer compatibility. This allows a larger processing window and restores some elongation. Yet the hydrated fillers remain unsuitable for insulation particularly in applications such as XHHW, RHH, SIS, and USE where wet dielectrics and insulation resistance are critical. Hence halogenated additives are still preferred in these applications.

However, there remain some formulation drawbacks in using halogen additives. The levels of halogen/antimony oxide to provide good flame retardance are in the 20-30% range. This implies that the polymer content is about 60% when all other minor components are included (peroxide, AO's, processing aids, pigments, etc.). Because PE is such a good fuel source (H/C greater than 2), compounds containing more than 50% PE are difficult to pass vertical burn tests. Test failure usually occurs when flaming particles drip and cause the cotton to ignite below. To overcome this deficiency 20-30% of inert fillers such as talc or calcium carbonate are required. The filler improves FR by acting as both a resin diluent and reinforcing agent to reduce dripping. Consequently some processability and physical properties are compromised. Optimization of this type of compounds is, therefore, always a balance of FR, processing and physical properties.

Formulations containing AO3, BR-I, and an inert filler were optimized to achieve UL94 V-0 and acceptable tensile/elongation properties. The samples also contained 100 ppm Cu and aged at 180°C to insure there is no detrimental effects to the AO system. The results are given in Table 5. Two BR-I levels were used. The incentive to try a lower level (less than 10%) was for economic reason since the FR package usually is the highest cost component in the formulation. As the result indicates, it is essential to have FR levels greater than 10% to achieve a V-0 rating although at higher filler level (35%) a V-I rating was obtained with the lower FR level. It is also encouraging that heat-aging performance remained suggesting the new AO system was not detrimentally affected by the filler.

TABLE 5: FR OPTIMIZATION

SAMPLE	RESIN	BR-I LEVEL	FILLER	UL 94	T/E	HEAT AGE
1	36.7	Normal	35	V-0	2400/440	20
2	41.7	Normal	30	V-0	2400/530	20
3	46.7	Normal	25	V-1	2390/640	19
4	41.9	Low	35	V-1	2420/500	18
5	46.9	Low	30	F	2330/560	19
6	54.9	Low	25	F	2330/710	16

The optimization of BR-I and A03 in EnBA formed the basis of an experimental 150°C compound. The critical properties in long term heat aging are outlined in Table 6 in addition to the FR and cure requirements for this application.

TABLE 6: 150°C RATED COMPOUND PROPERTIES

CURED PLAQUE		TARGETED WIRE PROPERTIES
1,830 PSI	Unaged Tensile	>1,800 psi
302%	Unaged Elongation Aged Elongation	>250%
92%	7 Days @ 180°C @ 158°C 90 Days 120 Days 150 Days Mandrel	>85% Retention >70% Retention >85% Retention from 90 Days >85% Retention from 120 Days Pass 150 Days
UL94-V-0	Flame Test	VW-1
0%	Heat Deflection	<15%

The material properties of the experimental compound are also included for comparison. However, It is important to recognize that finished wire properties are often different from cured plaque due to the impact of processing. Both line speed and temperature profile can cause substantially different cure characteristics. Incorrect temperature profile can result in loss of stabilizers and polymer degradation that will diminish heat aging performance.

WIRE PROPERTIES OF 150°C RATED COMPOUND

A test run of the experimental 150°C compound was carried out on a commercial-scale wire line using typical process parameters for this product. A #18 AWG tin coated copper wire was insulated with 30 mils wall at 400, 500, 600 ft/min line speeds. The compound extruded well with a glossy surface with no detectable difference at different line speed. The head pressure also was normal (<3000 psi) indicating proper filler loading and dispersion. No premature crosslinking (scorching) was observed. Overall, the processability was deemed excellent.

Stripped insulation samples were aged at 158°C for 150 days. Concomitantly wire samples were coiled around a small metallic cylinder and tested for cracks under the same condition (mandrel test). A commercial 150° C rated wire was also prepared and tested simultaneously. Additionally, wire samples were tested for VW-1, gel content, and heat deformation. The results are given in Table 7.

TABLE 7: 150°C RATED WIRE PROPERTIES

Unaged Tensile Strength	1,400 psi	
Unaged Elongation (break)	320%	
Tensile/Elongation @ 158°C		
30 Days	1,960 psi/200%	
90 Days	1,900 psi/170%	
120 Days	1,560 psi/140%	
Mandrel Test	Passed 120 Days	
	Failed 150 Days	
Competitive 150°C	Failed 90 Days	
FlameTest	Passed VW-I	
LINE SPEAD	GEL CONTENT	HEAT DEFORMATION
400 ft/min	43%	69.4%
500 ft/min	37%	72.9%
600 ft/min	22%	96.5%

It is important to note that both our experimental compound and commercial wire failed the long term heat aging test. The experimental compound performed better (failed at 120 days) compared to the commercial sample (90 days). It is also evident that our wire was undercured based on the gel and heat deformation data.

The deficiencies in our experimental compound are attributable to insufficient stabilization and peroxide loss during processing. Theoretically, heat stability can be improved by higher AO levels. However, it is not recommended in crosslinkable compounds due to the detrimental interaction with peroxide. Most antioxidants function by deactivating free radicals which is in direct conflict with peroxide action to generate free radicals. Mere addition of more AOs would only result in poorer cure with little or no improvement in heat aging.

OPTIMIZATION OF HEAT STABILIZATION AND CURE

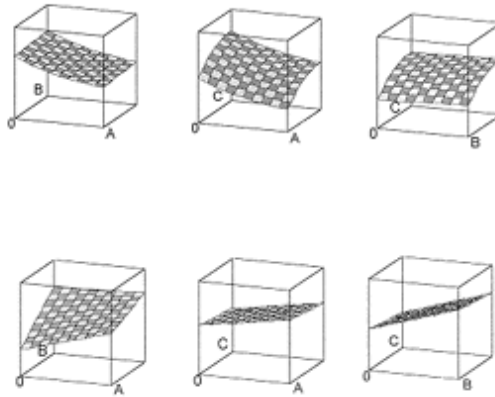
The AO-peroxide antagonism required a change in design strategy to improve both cure and heat stabilization. The antioxidant system, which is multi-component, was examined further to identify the free radical scavenging component. This component is denoted A and the other components are denoted B. The chemical curing system was also modified to improve cure. A cure coagent (C) was used to increase crosslinking rate without causing extensive AO interference.

TABLE 8: 3-FACTOR 3-LEVEL BOX-BEHNKEN DESIGN

RUN	PATTERN	A	B	C	ODR	HEAT AGE
1	--0	M	L	0	21	23
2	-+0	M	L	H	64	28
3	+-0	M	H	0	32	41
4	++0	M	H	H	67	39
5	0--	L	M	0	53	35
6	0-+	H	M	0	17	36
7	0+-	L	M	H	85	32
8	0++	H	M	H	54	37
9	-0-	L	L	L	75	25
10	+-0	L	H	L	80	38
11	-0+	H	L	L	46	35
12	+0+	H	H	L	45	41
13	000	M	M	L	54	37
* 14	000	M	M	L	57	37
* 15	000	M	M	L	58	35
* 16	++0	M	H	H	64	40
* 17	0-+	H	M	0	17	39
* 18	-0-	L	L	L	77	26

*** REPLICATES**

The components A and B from AO3, and C were optimized for 180°C oven aging (day) and Monsanto oscillating disk rheometer (ODR) measurement based on a 3-factor, 3-level Box-Behnken design. Experimental design can be used in formulation and development programs, not only to derive optimized formulations but also to detect and measure interaction between components.⁹ The Box-Behnken design is particularly useful to generate response surfaces such as heat aging and ODR for a set of continuous factors such as A, B, and C. These response surfaces, when projected onto the component planes, define the ranges of components for optimization. The levels are designated L (low), M (medium), and H (high) for the AO's and 0 (none), L, and H (high) for the coagent. The design pattern and the data obtained are given in Table 8.



The response surfaces derived from these data are graphed as a function of two factors giving rise to three surfaces for ODR and heat age. They are shown respectively, in Figure 1 and 2.

FIGURE 1: ODR RESPONSE SURFACES

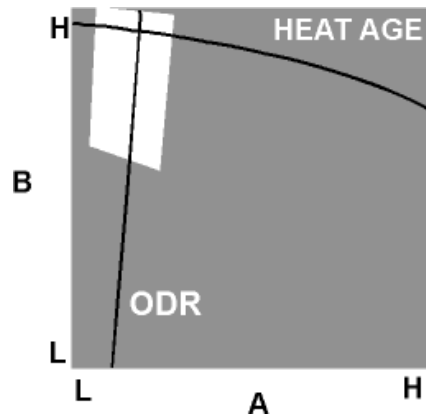
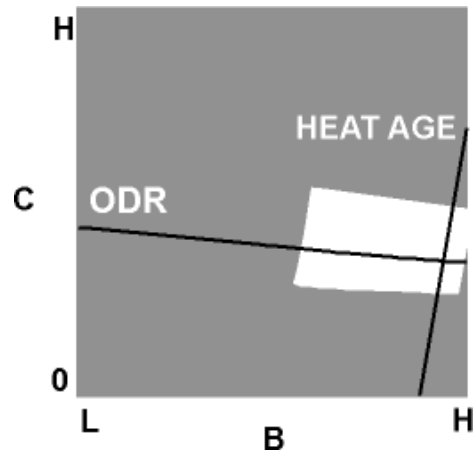


FIGURE 2: HEAT AGE RESPONSE SURFACES



A prediction profile and coefficients for the components are also derived for each property (Figure 3 and 4).

FIGURE 3: ODR PREDICTION PROFILE

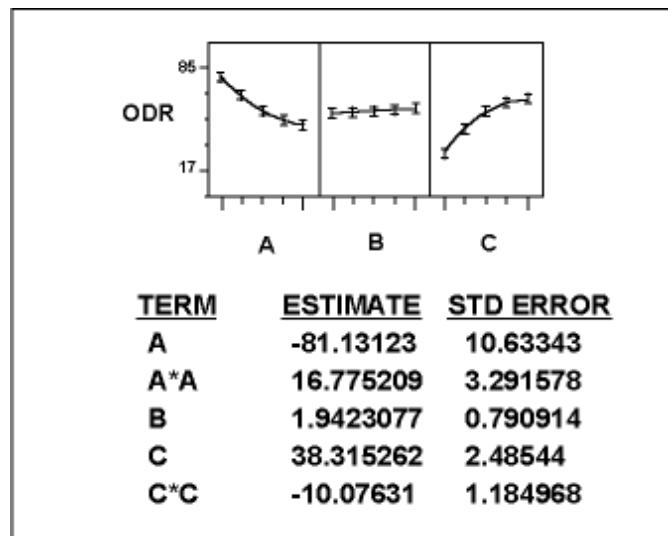
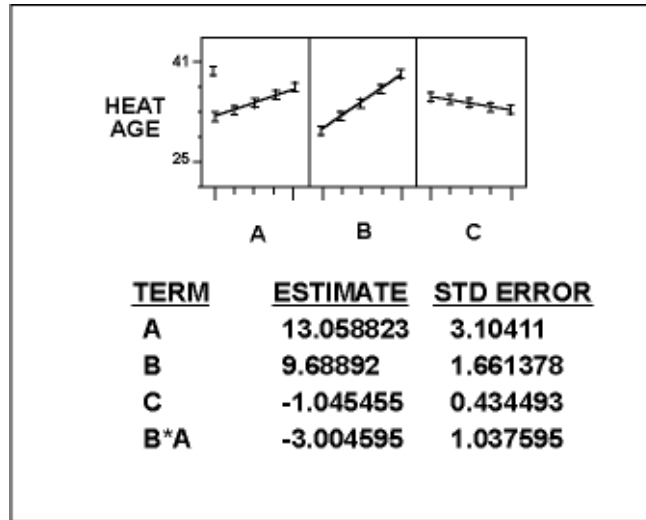


FIGURE 4: HEAT AGE PREDICTION PROFILE

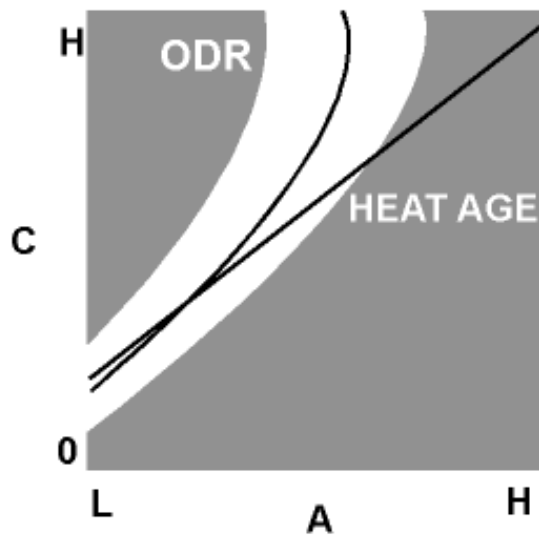


As expected, heat age is positively dependent on the AO system (A&B) while the cure coagent has a slight negative impact. For ODR, it is clear that C is the main contributor to cure. But more interestingly, negative response for A and the relatively weak or lack of dependence on B verifies the hypothesis that component A is the cause of free radical consumption.

Conceptually, optimization of the components points to a formulation that maximizes B for heat age and balances between A and C to obtain reasonable cure. Targets of 60-70 ODR and 35-40 days heat age were used for optimization. The basis for the ODR value is from independent gel and heat deformation experiments that cure was shown to be sufficient. The length of heat age is estimated from a 50% improvement on the previous material which had a 21 day accelerated heat age that corresponded to 120 days long term.

These targets define regions in the component planes (AB, AC, BC) shown as white areas in Figure 5.

FIGURE 5: OPTIMIZED ODR & HEAT AGE



Projection of the ODR and heat age surfaces onto these regions determines the component levels to achieve these values. The intersection of the projected curves for each component plane defines the levels for the two components. The three intersected points in Figure 5 corresponds to a unique set of A, B, and C. The predicted ODR and heat age for this set are 64 and 39 days, respectively.

The improved formulation based on the experimental design was compared to the previous material in ODR and 180° C heat aging. The result is shown in Table 9. It is clear that both cure and thermal stability were improved in the new formulation. Currently, the 158°C/150 day oven aging is being tested.

TABLE 9: IMPROVED ODR AND HEAT AGING

150°C	ODR	ACCELERATED HEAT AGE
Old	30 – 35	21 Days
New	60 – 65	30 – 35 Days

SUMMARY

A peroxide crosslinkable compound suitable for the 150°C rated appliance insulation was developed. The design combined screening of AO, FR, and base resin to derive the formulation. Laboratory studies showed that the presence of copper metal degraded thermal stability 20-50% in accelerated oven aging. Commonly used metal deactivator such as Irganox 1024 is effective at lower temperatures but not useful in higher temperatures up to 180°C. Certain brominated FR additives enhance the compound's thermal stability most likely due to some oxygen and nitrogen containing impurities that could act as copper chelating agents. A proprietary non-phenolic AO system was developed to provide the long term thermal stability. Its components and a cure coagent were optimized through a Box-Behnken experiment design for cure and heat aging. Wire samples exhibit good processability and superior long term heat aging performance when comparing to a commercial product.

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