

## Increase of rosin ester shelf life: Improvement of oxidative stability

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### ABSTRACT

The pentaerythritol rosin ester is a type of resin applied fundamentally in the constitution of adhesives. The growing competitiveness in the market of adhesive requires raw materials that are of high quality, of lighter color, even colorless, and remain so for long periods. However, rosin esters have a natural propensity to oxidize and darken, thus limiting their application. The aim of the present work was to suggest measures to increase the oxidative stability of pentaerythritol rosin ester produced by Respol Resinas, S.A.. Thus, various combinations of antioxidants were evaluated, and it was necessary to develop previously a laboratory method to incorporate them into the resin. The tested antioxidants were as follows: Irganox 245, Irganox 1010, Irganox 1425, Irganox 1726, Irgafos 126, Irgafos 168 and Lowinox TBM-6. Additivated resins were aged in an oven at 170°C and the results showed that the Irganox 1726 stabilizes better than the homologous antioxidant currently used in production, effectively retarding the darkening of the resin. Antagonisms were also diagnosed between species of antioxidants then used in production. The Irgafos 126 and 168 are not suitable for this material. In order to evaluate the effect of oxygen in the reaction medium on the resin color, esterifications were conducted on a laboratory scale using an inert gas (N<sub>2</sub>) with two different purities: 98% (available at the factory) and 99.999% (bottled). The results showed that the use of high-purity inert gas always gives lighter color resin with greater oxidative resistance. The use of antioxidant Lowinox TBM-6 during the esterification was crucial to maintain the low color resin.

**Keywords:** rosin, pentaerythritol ester, oxidative stability, antioxidant, adhesive, esterification.

### 1. Introduction

Rosin is a natural product obtained from living trees (gum rosin), from pine stumps (wood rosin) and from alkaline extraction of wood during Kraft pulping process (tall oil rosin) [1,2]. At room temperature, rosin is a resinous solid, vitreous and brittle whose color ranging from light yellow to reddish yellow. It has a softening point of about 70°C and is insoluble in water but soluble in most organic solvents [1,3]. Rosin is mainly composed by a mixture of diterpene monocarboxylic resin acids (about 90%), with a typical formula C<sub>19</sub>H<sub>29</sub>COOH, a certain quantity of fatty acids (in tall oil rosin) and a small fraction corresponding to neutral compounds, non-volatile and insaponifiable [2,4]. Resin acids are divided in four classes, depending on their molecular structure: abietic, pimaric, isopimaric (pimaric isomers) and labdenic. In Table 1 there's a composition in resin acids of two types of rosins.

Table 1

Compositions (% w/w) of rosins in resin acids [5].

Rosin Acids	Gum Rosin (Portuguese)	Tall Oil Rosin
Abietic	30,1 %	44,3 %
Neoabietic	17,5 %	4,2 %
Levopimaric + Palustric	22,1 %	7,7 %
Dehidroabietic	7,2 %	21,7 %
Pimaric	10,1 %	2,8 %
Isopimaric	9,9 %	5,9 %
Sandaracopimaric	1,5 %	1,0 %
Others	1,6 %	12,3 %

Rosin's instability to oxidation (and photo-oxidation) and corresponding darkening is primarily concerned with this conjugated double bonds of abietic type resin acids [1,2,6]. Rosin oxidation is started by the initiation step, i.e. heat, UV radiation, shear stress or impurities, free radicals are formed and accelerate the degradation by a complex mechanism [1,6]. Hydroperoxides are generated and when they react originate further free radicals and products which darkens the rosin [7].

J. Minn [6] determined oxidative stability of most common resin acids using HPDSC (High Pressure Differential Scanning Calorimetry). In Table 2 the results are presented as "Oxidation Induction Time" (OIT), i.e., the time at which the sample oxidizes when it is subjected to an isothermic under high pressure oxygen atmosphere.

Table 2

Oxidative stability of some resin acids, determined by HPDSC [6].

Resin Acid Type	Resin Acid	OIT @ 100°C (min)
Abietic	Dehidroabietic	1536
	Abietic	1
	Neoabietic	1
	Levopimaric	1
	Palustric	32
Isopimaric	Isopimaric	80

Although being abietic type, dehydroabietic acid does not contain conjugated double bonds and has a far higher oxidative stability.

Rosin may be esterified by reaction between resin acids carboxylic groups and polyalcohols hydroxyl groups, at

temperatures between 260 – 280°C. Pentaerythritol and glycerol are the most commonly employed alcohols [1,8,9]. During the esterification water is produced as a by-product and must be removed in order to displace the reaction equilibrium towards ester formation and thus allow the esterification to proceed. To prevent oxidation and darkening of the ester, the reaction is conducted under an atmosphere of high-purity inert gas [1].

Pentaerythritol and glycerol rosin esters are mainly used as tackifiers for hot-melt and pressure sensitive adhesives, and can also be applied in solder flux, as neutralizers in paper industry, in the formulation of chewing gum, etc. [9,12].

Similarly to rosin, these esters have a certain tendency to oxidize, become dark and lose their adhesive properties, thus limiting their application, since the adhesives industry require raw materials increasingly clear and stable. In fact, after rosin esterification, the resin acids conjugated double bonds (active sites for reaction with the oxygen) remains unchanged and thus available to react with oxygen [1,2,6]. Oxidation mechanisms for pentaerythritol rosin esters and other esters, were not found in the literature. However, the permanence of the active sites for the oxidation of resin acids after esterification, suggests that the oxidation mechanisms of pentaerythritol esters are analogous to those of rosin oxidation mechanisms. In this case oxidation may occur at lower rate, since the oxygen access to the unsaturation of resin acids is difficult by steric hinderance of esters bonds.

There are various methods to improve the oxidative stability of pentaerythritol esters: stabilizing the rosin (raw material) by isomerization/disproportionation and hydrogenation reactions; adding antioxidants during esterification and through the use of high-purity inert gas (N<sub>2</sub>).

The disproportionation reaction of rosin is generally understood as an exchange of hydrogen atoms between molecules of rosin's resin acids, whereby some resin acids are dehydrogenated and others hydrogenated [2,4]. In the presence of a catalyst (the most common is Pd/C), at temperatures between 200 and 270°C, the isomerization's resulting abietic acid of the other acids is dehydrogenated, forming the dehydroabietic acid, the most abundant component that gives the exceptional oxidative stability to the disproportionated rosin [2,4]. On the other hand, hydrogen atoms are preferably transferred to the vinyl group of the pimaric-type acids, structures very susceptible to hydrogenation, thereby forming the most stable dihydropimaric acids [2,4]. In Fig. 1 stands the reaction network for catalytic isomerization and disproportionation of rosin over Pd/C catalyst.

The rosin's oxidative stability can be effectively increased by the elimination of the conjugated double bonds of abietic type resin acids, resorting to hydrogenation reactions – the excellence method to stabilize rosin [1,10,11]. Hydrogenation of rosin is carried out at temperatures between 220 and 270° C, under high

pressure (between 12 and 35 MPa) and in the presence of noble metal catalysts such as Pd/C and Rh/C [1,10]. Due to the double conjugated bond's high reactivity, abietic-type acids are partially hydrogenated with relative easiness, forming dihydroabietic acids, as shown in Fig. 2. The vinyl group of pimaric type acids are also easily hydrogenated, producing dihydropimaric acids. It is also possible to get totally hydrogenated structures - tetrahydrogenated, but for this are required very severe operating conditions, namely higher pressure and higher hydrogen concentration in the medium [1,10]. Perform esterification with disproportionated or hydrogenated rosin originate esters with greater oxidative resistance as resin acids which not contain the reactive conjugated double bonds neither other unsaturation's [11].

The addition of antioxidants from the first stages of the manufacturing process is a method commonly used in the industry of polymers and resins to increase the thermal stability and photosensitive resistance of the products. In addition, the antioxidants play an important role in preserving the adhesive and rheological properties of the adhesive (main application of pentaerythritol esters) during their processing and shelf life, which is crucial to guarantee the excellence of the required quality standards in the industry. There are two main groups of antioxidants, distinguished by the resin oxidation inhibiting mechanism: primary and secondary antioxidants [7]. Primary antioxidants, such as sterically hindered phenols, deactivate free radicals (RO•) formed during thermal oxidation and interrupt breakdown reactions via a kinetic mechanism. They work by donating hydrogen atoms to preferably oxygen-centered radicals (RO•, ROO•), thereby interrupting the autoxidation process of the resin [7,13,14]. Secondary antioxidants, such as phosphites and tioethers, decompose peroxides (ROOH) formed during the autoxidation process and extend the performance of primary antioxidant by synergistic effects [7,13,14].

Finally, the esterification process must be conducted in total absence of oxygen, in order to prevent product oxidation [1]. Even in trace concentrations, oxygen dispersed in the reaction medium, in combination with the high reaction temperatures (260-280°C), causes a rapid oxidation of the product with subsequent darkening. Thus, use of high-purity inert gas (N<sub>2</sub>) is crucial to ensure a light color in the final product [1].

This work aims to evaluate various combinations of antioxidants, measuring its ability to slow resin darkening. Tests will also be performed to evaluate the inert gas quality effect in pentaerythritol rosin esters color, during esterification. The increase of pentaerythritol rosin ester oxidative stability by treatment of raw material (rosin) by disproportionation and hydrogenation, although promising, will not be discussed at this time.

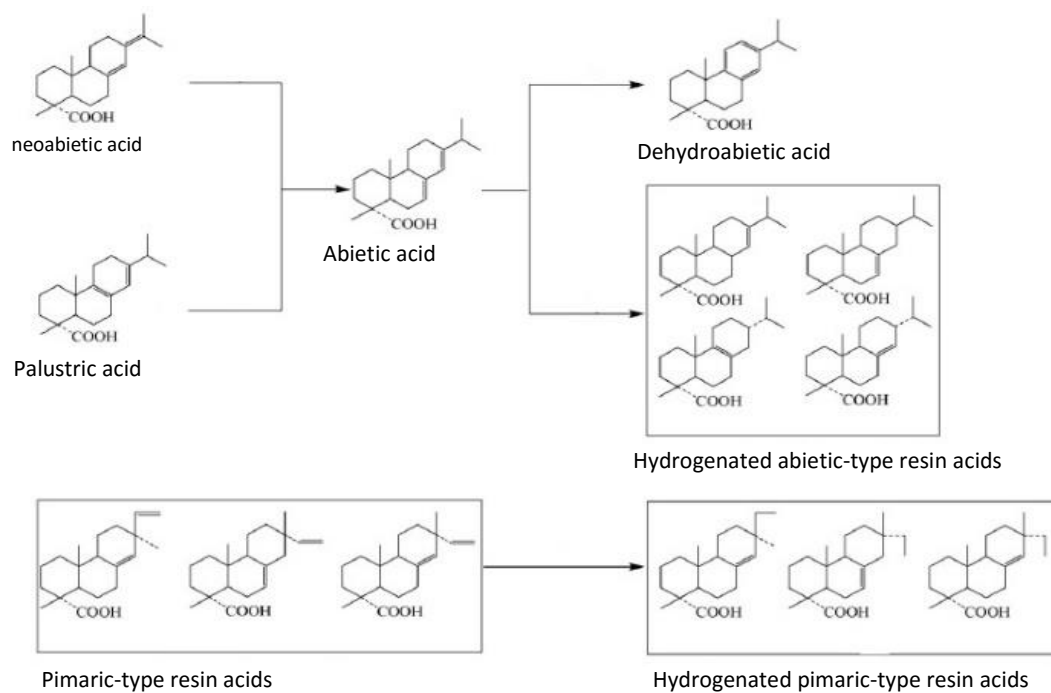


Fig. 1. Reaction network for catalytic isomerization and disproportionation of rosin over Pd/C catalyst [4].

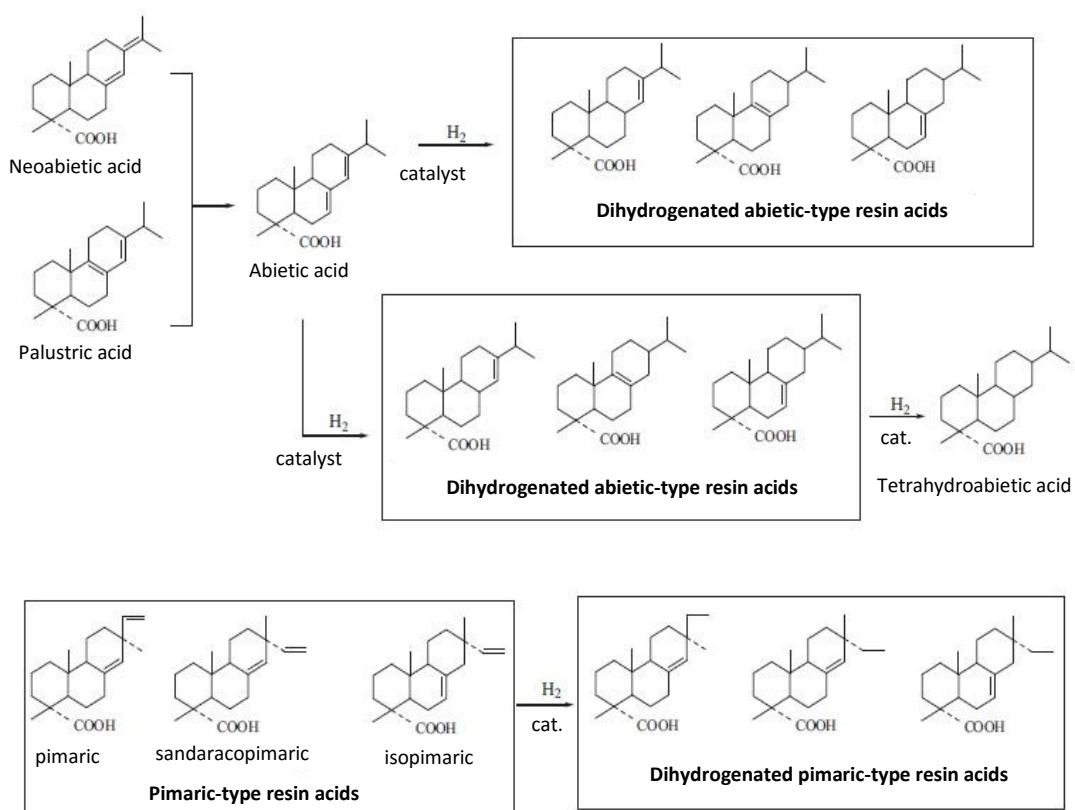


Fig. 2. Reaction network for catalytic hydrogenation of rosin [10].

## 2. Experimental

This work involves two distinct activities (Antioxidants evaluation and Inert Gas Tests), so that will be addressed separately in the next points.

### 2.1. Materials and Chemicals

For antioxidants trials, 20 kg of pentaerythritol rosin ester without antioxidants was obtained from Respol Resinas, S.A. Its softening point is 100 °C and a Gardner color of 3,0. The antioxidants Irganox 245, Irganox 1010, Irganox 1425, Irganox 1726, Irgafos 126 and Irgafos 168 were generously supplied by BASF. Lowinox TBM-6 was kindly provided by Addivant.

For inert gas tests technical grade Pentaerythritol and Tall Oil rosin was obtained from Respol Resinas, S.A.. Tall Oil rosin has a Gardner color of 2,8 and an acid value of 173 mgKOH/g. A 5.0 purity nitrogen bottle was purchased to Linde Group. In Table 3 are the purity grades of the two inert gases used in this activity.

Table 3

Purity of the two inert gases used in laboratorial esterifications.

Inert Gas	Purity (%)	O <sub>2</sub> (ppm)
Industrial	98	20 000
High Purity (N <sub>2</sub> – 5.0)	99,999	10

### 2.2. Experimental Setup and Procedure

First of all it was necessary to make the addition of antioxidants formulas into the pentaerythritol rosin ester (all antioxidant formulas used in this assessment are listed in Table 4). For this, it is used the Thermotronic II - an automatic varnish cooker, which made the incorporation of antioxidants formulas in 50g of resin at 200°C and 1000 rpm for 3 minutes, each run. Pentaerythritol rosin ester, antioxidants and a magnetic stir bar are charged into a proper metallic tube, which is then placed in the Thermotronic oven. After the end of the cooking program, additivated resin was discharged into aluminum bowls. These aluminum bowls containing additivated resin were then aged in a

Table 4

List of antioxidant formulas, mode of action and the concentration used in % (w/w).

Antioxidant	Action mode	1st Round Trials								2nd Round Trials								3rd Round Trials							
		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	E+	E++	F+	G+	H+	K+	K++	Q
Irganox 1010	Primary	0.25	0.25	0.80			0.80					0.25				0.25	0.25		0.25			0.25	0.25	0.50	0.50
Irganox 1425	Double functionality (Phosphite)				0.25	0.25		0.50	0.8			0.25						0.25	0.25		0.25	0.25	0.25	0.25	
Irganox 1726	Double functionality (Thioether)	0.50		0.50	0.50					0.50	0.50	0.25	0.75	0.50		0.50	0.25								
TBM-6	Double functionality (Thioether)						0.50	1.00	1.00					0.25					0.50	0.50	0.25	0.25			
Irgafos 168	Secondary (phosphite)		0.50			0.50				0.25									0.50 + iron spheres						
Irgafos 126	Secondary (phosphite)									0.25					0.50			0.50					0.25	0.25	
Irganox 245	Primary															0.25									

ventilated oven for 24 hours at 170°C. During the aging period the resin gradually deteriorates. This degradation and therefore susceptibility to oxidation is evidenced by blackening of the resin. Thus, the resin is as stable as the lowest dimming.

In order to get a more detailed evolution of the analyzed parameters, especially the Gardner color, resin samples are taken corresponding to intermediate periods, i.e. at 4, 8 and 24 hours of oven aging. Thus, it is possible to trace the aging curves expressing the variation of a given parameter as a function of time.

In inert gas tests, esterifications were performed between 260°C and 275°C, into a 500 mL flat bottom glass flask reactor. The temperature was continuously measured and controlled manually by acting on the heating plate. Agitation was promoted by using a stir plate and magnetic stirrer bar. The introduction of inert gas was made at the top of the reactor medium and its flow rate was defined and applied equally for all esterification's. The constituent parts of the unit were insulated with stone wool for thermal economy purpose. Besides medium inertization promoted by the inert gas, this acted as a drag agent of water vapor and other volatiles generated in the reaction medium to the outside.

In a typical trial, 271,25g of tall oil rosin were charged into the reactor, as well as magnetic stirrer bar and 1.36 g of antioxidants. The inert gas was turned on and after 5 minutes the heating and agitation plate was switched on. This was done to ensure that in reaction medium there's no dispersed oxygen. Agitation was set to 60 rpm. When the reaction mixture reached 218°C 28,75g of pentaerythritol (10,6% with respect to the initial tall oil rosin mass) was added. When it reached 250°C esterification of rosin with polyalcohol starts and is maintained for 4 hours or 6 hours. The resin produced is discharged into aluminum bowls and about 100g of resin are placed in a 400 ml glass beaker and is subjected to aging in a ventilated oven for 24 hours at 140°C. The experimental apparatus was ready to operate alternately with industrial inert gas and high purity inert gas (5.0 grade)

### 2.3. Sample Analysis

The Gardner color of the various additivated and aged resins were determined using a *Lico 620* colorimeter. Firstly a 50% (w/w) dissolution of resin in toluene was made and then was read in the instrument.

Resin viscosity was determined at 163°C using a *Brookfield* rotational viscometer with a *Thermoseal* thermostatic chamber. These analyzes were performed according to the Respol laboratory procedures.

The Gardner color of 10 pentaerythritol rosin esters before and after aging were determined by the same manner as described in first paragraph 2.3. Sample Analysis.

For the sake of comparison of the various synthesized resins, acid's concentration (acid number) were also analyzed by direct basic titration, based on the ASTM D 1639-90. In this method, a freshly made KOH 0,5N solution in methanol standardized is employed to titrate about 3g of the sample solubilized in 100 mL of 2:1 (v/v) toluene and diacetone alcohol solution with a drop of phenolphthalein (10g/L in ethanol).

### 2.4. Gardner Color Values Treatment (Antioxidant Evaluation)

In order to facilitate interpretation and clear comparison of different formulations of antioxidants, Gardner color values obtained for the various additivated and aged resins were converted to the respective variation (in percentage) relatively to the original properties of the resin. The conversion was made by the use of following equation (Eq. 1):

$$\text{Gardner Color Variation (\%)} = \frac{\text{Color (4h, 8h or 24h)} - \text{Color (0h)}}{\text{Color (0h)}} \times 100 \quad (\text{Eq. 1})$$

In Table 5 there is an example of the resulting conversion of formula R color data.

**Table 5**  
Conversion of Gardner color values to respective variation, in percentage (%).

Hours of Aging	0h	4h	8h	24h
Gardner Color	3,1	8,0	9,2	14,6
Variation (%)	0	158	197	371

## 3. Results and discussion

### 3.1. Antioxidants Evaluation

#### 3.1.1. The best antioxidants formulas

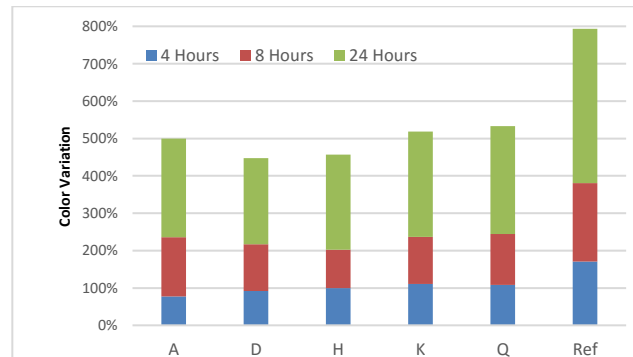
In Table 6 are the best formulas of this activity, i.e., those formulas which allowed a lower degradation of the resin (indicated by color variation). The mentioned formulations exhibited good performance during all three periods of aging, showing the continuing action of the antioxidants throughout the test.

**Table 6**  
The best formulas of antioxidants and their constitution.

Formula	Antioxidant 1	Antioxidant 2	Antioxidant 3
A	Irganox 1010	Irganox 1726	-
D	Irganox 1425	Irganox 1726	-
H	Irganox 1425	TBM-6	-
K	Irganox 1010	Irganox 1726	Irganox 1425
Q	Irganox 1010	Irganox 1425	-

Antioxidants that arise most often in these formulas are Irganox 1425 and Irganox 1726. The latter is a new antioxidant that had not yet been tested in the pentaerythritol rosin ester of Respol and shows promising results.

In the bar graph of Fig. 3 a comparison between resins additivated with the best antioxidant formulas and one resin without antioxidants (Ref) is made.



**Fig. 3.** Aging comparison between resins additivated with the best antioxidant formulas and a free-antioxidant resin.

The results shows that additivated resins have higher resistance thermal/oxidative in relation to non-additivated resin, preventing color degradation by about 35%.

#### 3.1.2. Comparison between Irganox 1726 and TBM-6

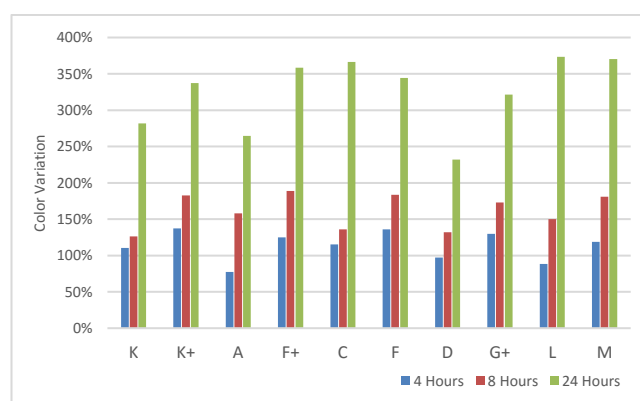
The Irganox 1726 and TBM-6 have double functionality (primary and secondary actions) and have a thioether structure. Irganox 1726 has a substantially higher molecular weight than the TBM-6, 537 and 358 g/mol, respectively. This is an interesting property in a potential industrial application where high molecular weights are preferable.

Four pairs of formulations were made which allow a direct and clear comparison of the action of the two antioxidants in discussion. In each pair of formulations varies only the

antioxidant with thioether structure. The pairs of formulas to consider in the comparison are shown in Table 7 where reference is made to the antioxidant species and concentrations used in each formula, and in Fig. 4 there is a graphical comparison.

**Table 7**  
Antioxidant formulas used in performance comparison of Irganox 1726 and TBM-6.

Formula	Irganox 1726	Other Antioxidants	Formula	TBM-6	Other Antioxidants
K	0,25%	0,25% Irganox 1010 0,25% Irganox 1425	K+	0,25%	0,25% Irganox 1010 0,25% Irganox 1425
A	0,50%	0,25% Irganox 1010	F+	0,50%	0,25% Irganox 1010
C	0,50%	0,80% Irganox 1010	F	0,50%	0,80% Irganox 1010
D	0,50%	0,25% Irganox 1425	G+	0,50%	0,25% Irganox 1425
L	0,75%	-	M	0,25%	0,50% Irganox 1726



**Fig. 4.** Performance comparison of Irganox 1726 and TBM-6 in aging of additivated resins.

The results shows consistently that when TBM-6 composes a formula, thermal/oxidative resistance is lower than the analogous formula comprising Irganox 1726, thus demonstrating the supremacy of the latter antioxidant.

This comparison provides a strong evidence that the antioxidant Irganox 1726 performs a protection of the pentaerythritol rosin ester substantially higher than Lowinox TBM-6, constituting an alternative to consider in posterity.

### 3.1.3. Antagonism

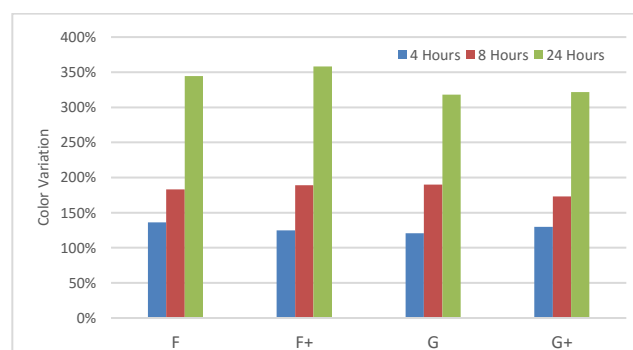
First, the comparison of two antioxidants made in Fig. 4 indicates a low TBM-6 compatibility with other antioxidants in the resin. In fact, TBM-6 can be in antagonism with other antioxidants, namely with Irganox 1010 and Irganox 1425, there arises the reason it is inefficient when constitutes a formula.

Going further with this suspicion, the pair of formulas F and F+ shows the relationship between TBM-6 and Irganox 1010 and the pair of formulas G and G+ highlights the relationship between TBM-6, and Irganox 1425 (see Table 8).

**Table 8**  
Antioxidant formulas containing TBM-6 in antagonism with other antioxidants.

Formula	TBM-6	Other Antioxidants	Formula	TBM-6	Other Antioxidants
F	0,50%	0,80% Irganox 1010	F+	0,50%	0,25% Irganox 1010
G	1,0%	0,50% Irganox 1425	G+	0,50%	0,25% Irganox 1425

Generally, the higher the antioxidant concentration, the greater the ability to stabilize the resin. However, in few cases very high concentrations of antioxidants may have reverse action [7]. Thus, formulas F+ and G+ have a lower antioxidant levels to outwit this hypothesis. Fig. 5 outlines the results of the aging of additivated resins with these four formulas.



**Fig. 5.** Comparison of additivated resins with antioxidant formulas generating antagonism.

The color evolution of resins additivated with formulas F and F+ are very similar, showing that resins have an identical resistance with either 0,8% or 0,25% of Irganox 1010. The TBM-6 content in both formulas remained (0,50%) and most likely inhibit the action of Irganox 1010. Analogously, changes in color of additivated resins with G and G+ formulas also suggest conflict between the two antioxidants (TBM-6 and Irganox 1425), since degradation of the resin is identical, regardless of their contents. Lastly, the possibility of formulas inefficiency due to very high concentrations of antioxidants was eliminated and the antagonistic relationships between TBM-6 and Irganox 1010 and 1425 were disclosed.

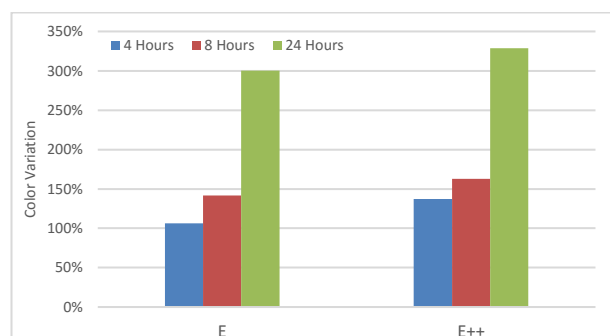
### 3.1.4. Secondary antioxidant action

At the beginning, the expectation on the performance of these substances (Irgafos 126 and Irgafos 168) was high given its main function - confer oxidative stability at high temperatures. However, aging methods revealed that the joint action of these antioxidants with others generated poor oxidative resistance. Furthermore, Irgafos are not specifically recommended by the manufacturer for use in rosin esters. It is necessary to develop a new molecule with a structure based on phosphite compatible with pentaerythritol rosin esters, since there is no alternative product currently on the market.

### 3.1.5. The effect of a free radical precursor

To evaluate the effect of free radical precursors trace amounts in resin oxidation stability, 2 tiny iron balls (diameter  $\pm$  2 mm) were placed in each of the aluminum bowls containing

additivated resin with E formula (constituting E++ formula). Afterward, these resins were aged according with typical procedure and the results are shown in Fig. 6 and compared with a resin free of oxidation precursors (E).



**Fig. 6.** Disclosure of the effect of a precursor of free radicals in resin degradation (E++).

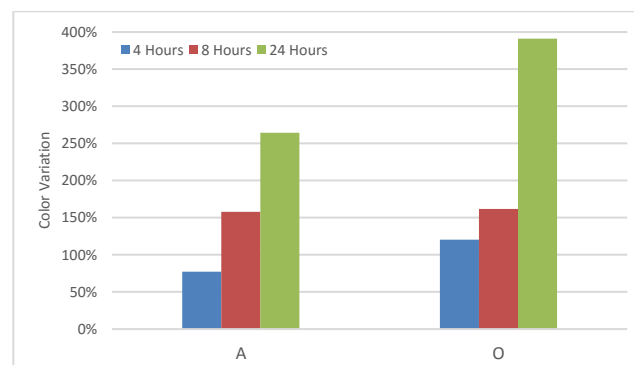
It is notable that the presence of iron during aging process boosts the oxidation of the resin (E++), with a more pronounced darkening in the three test periods. The iron as free radical producing catalyst causes an overload of the primary and secondary action of Irganox 1425 and Irgafos 168. This led to a quickly consumption of antioxidants with subsequent end of resin protective action.

It proves that the presence of free radical precursors, such as iron and many others, have an adverse effect on resin oxidative stability and it is imperative to prevent its occurrence.

### 3.1.6. Comparison between Irganox 1010 and Irganox 245

In the graph of Fig. 7 is made the comparison of two primary antioxidant: Irganox 1010 and Irganox 245. The

formulas A and O are made up of 0.25% of Irganox 1010 and 0.25% Irganox 245, respectively.



**Fig. 7.** Performance comparison of Irganox 1010 (A) and Irganox 245 (O) in aging of additivated resins.

For the analysis of the results it is clear that the Irganox 1010 (Formula A) is more efficient in resin oxidation prevention than Irganox 245 (Formula O). This is due to the fact that the Irganox 1010 has about twice the molecular weight of Irganox 245 and the former has 4 hydroxyl groups (actuator in the suppression of free radicals) against 2 of the second.

It is also visible that the antioxidants of the formula O are consumed quickly within the period of 8 hours. From this point the resin is unprotected and darkens more intensely.

### 3.2. Inert Gas Tests

The main results for the ten esterifications are reported in Table 9. These tests also tested the efficacy of some antioxidants formulas in the esterification process.

**Table 9**

Main operation conditions and results of the laboratorial esterification's with industrial and high purity inert gases.

Esterification	Inert Gas	Antioxidants	Esterification Duration (h)	Average Temp. Esterification (°C)	Acid Number (mgKOH/g <sub>resin</sub> )	Gardner Color	Gardner Color After Aging
1	Industrial	0,15% Irganox 1425 0,35% Irganox 1010	4	269,6	39,3	6,1	7,5
2	High purity			265,3	51,2	5,6	6,5
3	Industrial	0,15% Irganox 1425 0,35% TBM-6	4	260,9	54,6	4,3	5,2
4	High purity			268,1	45,1	3,2	4
5	Industrial	0,15% Irganox 1425 0,35% TBM-6	6	270,2	33,1	4,4	4,8
6	High purity			266,2	33,8	3,8	4,2
7	Industrial	0,15% Irganox 1425 0,05% Irganox 1010 0,30% Irgafos 168	6	261,2	43,4	5,6	6,5
8	High purity			262,8	38,4	5,5	5,9
9	Industrial	None	6	268,4	37,7	7,3	8
10	High purity			264,1	41,7	6,3	6,9



During esterification process some temperature fluctuations were denoted, which caused some differences between the average temperatures of the esterification. Nevertheless, all the average esterification temperatures are within the target range 260 - 270°C.

The results are consistently conclusive: the use of high-purity inert gas in esterifications always allow the obtainment of lighter colored resins, comparatively to homologous esterifications with industrial gas. Furthermore, the resins produced with high purity inert gas, in general, suffered less degradation in color when subjected to oven aging. This is particularly noticeable by comparing the esters 7 and 8 which were produced with similar color. In fact, the presence of higher oxygen concentrations during the esterification has not only immediate influence on the resin color, as suggests an impairment of oxidative stability in further processing at elevated temperatures.

A brief note for antioxidants tested in this activity. Esters 3, 4, 5 and 6 produced with 0,35% of TBM-6 revealed the lighter colors, thus indicating the important role of this antioxidant in color retention, when applied at the beginning of the reaction. On the other hand, expectedly, the two resins synthesized without any antioxidant (9 and 10) had the highest colors. It was used in eight esterification's a fixed amount of 0,15% of Irganox 1425, because this substance besides acting in resin oxidative protection, also plays a catalytic role in esterification reaction.

#### 4. Conclusions

The main objective of the present work was to suggest actions to increase the oxidative stability of pentaerythritol rosin ester produced by Respol Resinas, S.A..

The antioxidants essays allowed to conclude that Irganox 1726 in combination with other kinds of antioxidants has a much greater ability to retard the darkening of the resin's color comparatively to the homologous antioxidant used in production. The replacement of the homologous by Irganox 1726 is now being implemented in production.

Antagonisms were identified in combined application of Lowinox TBM-6 with Irganox 1010 and Irganox 1425. Their combined use as final antioxidants addition in the manufacturing process of pentaerythritol rosin esters are not recommended.

The secondary antioxidants, Irgafos 126 and Irgafos 168, not effectively stabilized resin (allowing its pronounced darkening), so it is not recommended for use in rosin derivatives.

The use of high purity inert gas during esterification reaction allowed to obtain lighter colored esters and presumably higher oxidative resistance in subsequent processing at elevated temperatures. It is strongly recommended an improvement in inert gas quality used in the factory esterification reactions. With this tests it was also found that Lowinox TBM-6 antioxidant has a

remarkable ability to maintain the resins color always at low levels throughout the esterification. So his use is recommended from the beginning of the esterification (not as final addition).

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