

**HIGHER-SOLIDS, HIGHER QUALITY ACRYLIC COATINGS RESINS
PRODUCED WITH ORGANIC PEROXIDE INITIATORS**

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ABSTRACT

The initiator plays a dominant role in the free radical synthesis of higher-solids acrylic based coatings resins. Both the chemical nature of the initiator and the polymerization conditions greatly influence the efficiency of the polymerization and the final resin properties. Proper initiator selection results in acrylic high-solids coatings (HSC) resins with low molecular weight, narrow polydispersity, low viscosity, and reduced volatiles.

Reported are guidelines to improve acrylic HSC resin properties through a better understanding of organic peroxide structure/activity relationships and the use of statistical experimental design. These criteria were used to determine the optimum polymerization conditions and produce higher-solids, higher quality acrylic resins.

INTRODUCTION

The development of high solids coatings (HSC) resins in the United States was necessary to meet strict environmental regulations geared to reduce emissions of volatile organic compounds (VOCs). While Europe has lagged the U.S., similar regulations are being considered.¹ In certain solvent-borne formulations like acrylics, the VOCs can be reduced by reducing the solvent content; however, the product quality and performance must be maintained in the lower VOC content formulations. In order to achieve high solids formulations and ensure the lowest viscosity, acrylic polymers (or oligomers) with both low molecular weight and a narrow molecular weight distribution (MWD) must be used.² The most common method used to produce low molecular weight acrylic polymers is to employ high concentrations (up to 6%) of azonitrile or organic peroxide initiators, alone or in combination with chain transfer agents, and careful control over the process variables is essential.

While these efforts have been partially successful, limitations still exist. Many drawbacks are influenced by differences in free radical reactivity and associated structural features of the initiator. In classical free radical chemistry, the initiator is simply treated as "R•" and little consideration is given to the chemical nature of the R group, initiator decomposition mechanisms, and the type of radicals produced.

In recent years, organic peroxide initiators have become a dominant factor in the synthesis of low molecular weight, narrow molecular weight distribution acrylic HSC resins.³ Advances in organic peroxide technology such as t-amyl peroxides have led to a better understanding of the structure/reactivity relationships of the initiator and the effect on resin properties.^{4,5} Proper initiator selection can result in better controlling and lowering the molecular weight of the resin, decreasing the polydispersity, and increasing the solids level of the formulation.

This paper will report a comprehensive study on how the organic peroxide chemistry, decomposition mechanism, and rate of decomposition (half-life) can influence the initiator choice and the molecular weight properties of acrylic HSC resins. In addition, the use of experimental design to help optimize the polymerization conditions and initiator blending to improve productivity and HSC resin quality is discussed.

EXPERIMENTAL

High-solids, hydroxy-functional acrylic resins were prepared by conventional free-radical solution polymerization techniques. The polymerizations were conducted under nitrogen in a jacketed, 2L glass reactor equipped with a stirrer, thermometer, and reflux condenser. A monomer feed consisting of 40% butyl methacrylate (BMA), 25% butyl acrylate (BA), 25% 2-hydroxyethyl acrylate (HEA), 7.5% styrene (STY), and 2.5 % methacrylic acid (MAA) was used. The monomer mix and initiator were combined and metered into the reactor containing solvent at a prescribed temperature over a five hour period. After the monomer and initiator addition was complete, polymerization was

continued for an additional hour. The monomer to solvent ratio was 3.7 to 1 (80% solids theoretical). The solvent used was Aromatic 100™ (substituted benzenes - Exxon Chemicals).

All the organic peroxides were evaluated at their 15 minute half-life temperatures and an equal active $[O] = 0.42$ phm unless otherwise stated (see Appendix I). The azonitrile initiator was evaluated against each of the t-amyl peroxides at their 15 minute half-life temperatures and an equivalent active $[N]$.

The molecular weights of the acrylic polymers were determined by gel permeation chromatography using polystyrene standards. A Waters Associates Model 401 differential refractometer detector and three Styragel columns of 10^4 , 10^3 and 500 Angstroms were used. The solvent was tetrahydrofuran with a flow rate of 1.0 milliliter/minute.

The residual monomer content was measured using a Hewlett Packard model 5890 gas chromatograph with a flame integration detector. The BMA, EA, and STY were determined using a 30 meter DB-1 Megabore column (JW Scientific) with a 0.53 mm diameter and 1.5 μ film thickness. The MAA and HEA were determined using a 6', 10% SP-216 PS (Supelco) packed column. Percent total residual monomer reported is the sum of the five monomers determined.

RESULTS AND DISCUSSION

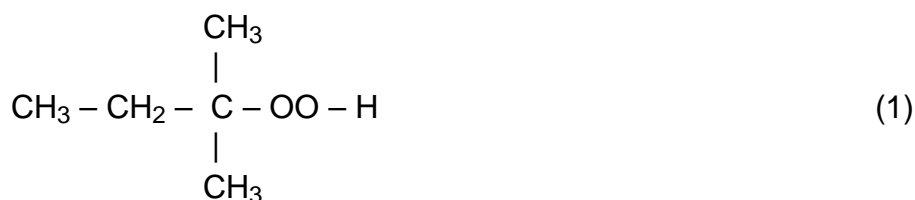
Background

Efforts in recent years have been directed toward the production of increasingly higher solids hydroxy-functional acrylic coatings resins to reduce emissions of volatile organic compounds. However, the required quality standards cannot be compromised, particularly with regard to appearance, physical properties, and performance. Current technology utilizes acrylic polymers of low molecular weight and a narrow MWD to obtain acceptable solution viscosity in the coatings formulation. In the synthesis of these resins, azonitrile and organic peroxide initiators in combination with high concentrations of a chain transfer agent are generally employed. However, there are drawbacks in current initiator technology for HSC polymerizations.

Azonitrile initiators are commonly used in the synthesis of high solids, low molecular weight acrylic resins, to obtain a narrow MWD and low solution viscosity. Azonitriles decompose to form alkyl radicals which are more selective and poor in hydrogen (H) abstracting ability. The H-abstracting ability of the free radicals generated from the initiator plays a major role in determining the polymer MWD. While azonitriles offer certain advantages, they also exhibit several disadvantages including: (1) they are solids and have limited solubility; (2) they have a limited activity range (half-life) and are generally used at very fast rates of decomposition, thus lowering the efficiency; and (3) they generate highly colored resin solutions.

Most conventional organic peroxides, in particular those derived from tertiary (t) butyl hydroperoxide, found themselves excluded from HSC polymerizations due to the highly reactive nature of the oxygen-containing radicals. Dialkyl peroxides for example are commonly used in the cross-linking of polyethylene and the vis-breaking of polypropylene.⁶ The primary mechanism involved is the H-abstraction of polymer hydrogens by the free-radicals generated from the peroxide. In acrylic HSC systems where a minimal amount of solvent is used, a similar analogy could be used. Free-radicals from the initiator may abstract hydrogens from the acrylic polymer which can lead to chain branching, a broader MWD, and higher solution viscosity. Therefore, chain transfer agents (e.g. mercaptans) are needed to lower the molecular weight; however, mercaptan chain transfer agents can produce objectionable odors, color, and light instability in the coatings.⁷

All of these drawbacks in conventional initiator technology for HSC polymerizations may be overcome with the use of organic peroxides derived from t-amyl hydroperoxide (1).



t-Amyl peroxides, like azonitriles, decompose to yield very selective radicals that are poor hydrogen abstractors as compared to conventional organic peroxide initiators. In addition, advantages are also realized over conventional azonitrile initiators. All the t-amyl peroxides are liquids with excellent solubility. They cover a wider activity range with greater efficiency and yield resins with lower color and lower residual monomer levels.

How The Initiator Type Influences the Molecular Weight

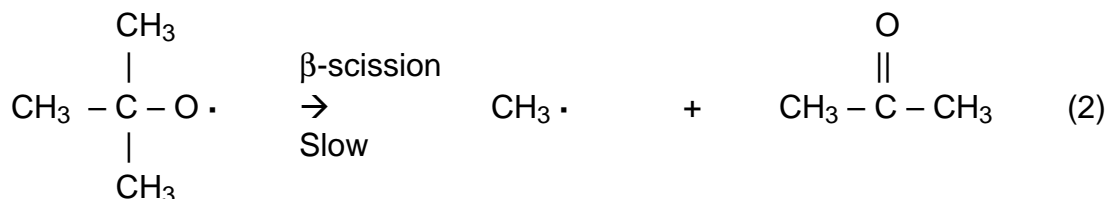
The primary factors that influence the molecular weight properties of acrylic HSC resins and the efficiency of the polymerization are the initiator concentration, initiator type and radicals produced, the rate of decomposition of the initiator, the polymerization temperature, the solvent type, monomer mix, and feed rate. Therefore, the initiator or initiator type in most cases is the dominant factor in controlling and lowering the molecular weight, decreasing the polydispersity (MWD), and increasing the solids content in the process.

The role of the initiator is related to the chemical structure and the types of radicals generated. Radical stability and reactivity are related to the hydrogen bond dissociation energy of the parent compound.⁶ Using the bond dissociation energy, radicals such as methyl, t-butoxy, alkoxy and phenyl are highly reactive and are good hydrogen abstractors. Conversely, radicals such as the ethyl, t-butyl, and isopropyl are lower in energy and are poor hydrogen abstractors. To illustrate, when t-alkyl peroxides, e.g. peroxyesters, peroxyketals, and dialkyls, are thermally decomposed, one or more

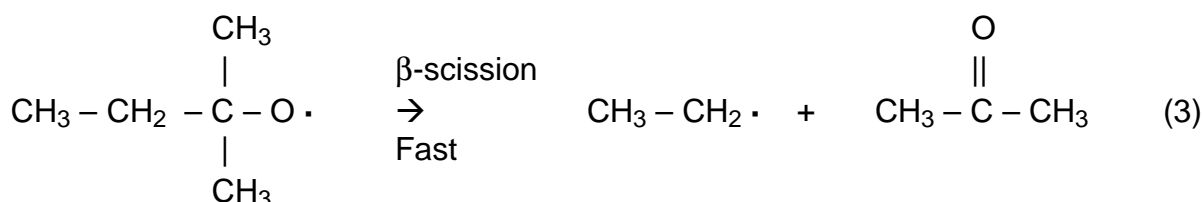
t-alkoxy radicals are formed. Comparison of the β -scission reaction for the t-butoxy radical and the t-amyl radical illustrates an important advantage for t-amyl peroxides (see Figure 1).

Figure 1 The β -scission reaction comparing the t-butoxy vs. the t-amyl radical

t-butoxy radical:



t-amyl radical:



t-Butyl peroxides decompose to form a t-butoxy radical (eq. 2). The β -scission reaction is slow and the predominant initiating species is the t-butoxy radical or, if β -scission occurs, the methyl radical. Both radicals are highly reactive and readily capable of H-abstraction. On the other hand, t-amyl peroxides decompose to form a t-amyl radical (eq. 3). The β -scission reaction is almost instantaneous to yield acetone and the ethyl radical. The ethyl radical is the predominant initiating species, and the relative stability of the ethyl radical minimizes H-abstraction. This decreased tendency toward H-abstraction leads to less long-chain branching, giving better control over molecular weight, MWD, and viscosity.

To illustrate the relative H-abstracting capabilities and the β -scission reaction between t-butyl and t-amyl peroxides, 5% solutions of di-t-butyl peroxide (DTBP) and di-t-amyl peroxide (DTAP) were decomposed in Aromatic 100. The by-products, t-butyl alcohol and acetone for DTBP and t-amyl alcohol and acetone for DTAP, were measured (see Table I).

Table 1 Decomposition by-products of di-t-butyl peroxide (DTBP) and di-t-amyl peroxide (DTAP) in Aromatic 100 solvent.

Peroxide/Conc. * (moles)	t-Butyl Alcohol (moles %)	t-Amyl Alcohol (moles %)	Acetone (moles %)
DTBP / (3.44E ⁻³)	84	--	18
DTAP / (2.86E ⁻³)	--	16	75

* 5% (wt) in solution

As can be seen in Table 1, the measured t-butyl alcohol accounted for 84% (mole fraction) of the initial DTBP and the acetone accounted for only 18% of the initial DTBP. For DTAP, the measured t-amyl alcohol accounted for only 16% of the initial DTAP and the acetone accounted for 75% of the initial DTAP. The amount of acetone measured indicates that the β -scission reaction is much faster for the t-amyl peroxide than the t-butyl peroxide. The amount of t-butyl alcohol and t-amyl alcohol indicates that more H-abstraction will occur (from solvent and/or polymer) using the t-butyl peroxide vs. the t-amyl peroxide.

Peroxide Selection

To a large extent, the decomposition rate at which an organic peroxide produces free radicals determines the application temperature and controls the overall polymerization efficiency. Decomposition rates of organic peroxides are commonly reported in terms of half-life ($t_{1/2}$) time or temperature, i.e., the time at which 50% of the peroxide has decomposed at a specified temperature or the temperature at which 50% of the peroxide has decomposed at a specified time, respectively. To aid in the selection of the optimum organic peroxide and half-life characteristics best suited for a particular polymerization temperature, ATOCHEM has available on computer diskette half-life data for most of the commercial organic peroxides.⁸ The HALFLIFE[®] program provides a rapid and accurate means for determining half-life temperatures or half-life times and % residual peroxide at various time/temperature profiles.

In most HSC polymerizations of acrylic monomers, the polymerization temperature is greater than 100°C and the organic peroxide is chosen so that the half-life time under the reaction conditions is in the range of 2 to 20 minutes. Therefore, the recommended t-amyl peroxides initiators for HSC polymerizations have 10 hour $t_{1/2}$ temperatures of > 70°C and are listed in Table 2⁹.

Table 2 t-Amyl Peroxides for HSC Polymerizations.

Code Name	Chemical Name	Half-Life ($t_{1/2}$), °C ¹		
		10 hr	1 hr	15 min
L575	t-Amyl Peroxy-2-Ethylhexanoate	75	92	103
L531 ²	1,1-Di-(t-Amylperoxy)Cyclohexane	93	112	124

TAEC	OO-t-Amyl O-(Ethylhexyl)Monoperoxy carbonate	99	117	129
TAPB	t-Amyl Perbenzoate	100	122	135
L555 ³	t-Amyl Peroxyacetate	100	120	134
L553 ⁴	2,2-Di-(t-Amylperoxy)Propane	108	128	142
L533 ⁴	Ethyl 3,3-D (t-Amylperoxy)Butyrate	112	132	145
DTAP	Di-t-Amyl Peroxide	123	145	157

¹ measured at 0.2 molar in dodecane

² offered as a 80% solution in odorless mineral spirits

³ offered as a 60% solution in odorless mineral spirits

⁴ offered as a 75% solution in odorless mineral spirits

Acrylic HSC Resin Properties

To illustrate the effect of initiator type, various acrylic HSC polymerizations were conducted comparing L575, L531, L555, L533, and DTAP against their t-butyl derivatives and a typical azonitrile initiator, 2,2'-azobis(methylbutyronitrile) (see Appendix I). All the organic peroxides were evaluated at their 15 minute half-life temperatures and an equal active [O] = 0.42 phm. The azonitrile initiator was evaluated against each of the t-amyl peroxides also at their 15 minute half-life temperatures and an equivalent active [N]. Note in Appendix I that most of the t-amyl peroxides also offer lower use levels (phm) at equivalent activity as compared to the azonitrile initiator which may improve the cost efficiency of the process.

Table 3 compares the number average molecular weights (Mn), MWD's, and solution viscosities at 75% solids of acrylic HSC resins produced from t-amyl peroxides against their t-butyl peroxide analogues. In all cases, the t-amyl peroxide produced resins had lower Mn's, narrower MWD's (Mw/Mn), and lower solution viscosities as compared to their t-butyl peroxide analogues. In some cases, the MWD was less than 2.0 and the viscosity was reduced 50% utilizing the t-amyl peroxide vs. the t-butyl peroxide. The improvement in molecular weight properties are directly related to the structural differences of the organic peroxides tested and illustrates the importance in considering the free-radical type as an integral part of experimental design.

Table 3 Molecular Weight and Viscosity Properties of Acrylic HSC Resins Synthesized with t-Amyl Peroxides vs. t-Butyl Peroxides

Initiator	Polym Temp (C)	Mn	Mw/Mn	Mz/Mn	Viscosity* (poise)
DTAP	157	2500	1.81	2.96	15
DTBP	162	3200	2.60	6.30	32

L533	145	2800	2.00	3.62	25
L233	147	3700	2.30	4.88	52
L555	134	3300	1.90	3.10	38
L70	136	3600	2.25	4.49	51
L531	124	4600	2.41	5.32	93
L331	128	5300	3.20	9.00	152
L575	103	6400	2.09	3.73	152
TBPO	106	6200	2.49	5.44	188

* Brookfield viscosity at 260°C and 75% solids content.

Table 4 compares the Mn, MWD, and solution viscosities of acrylic HSC resins produced from t-amyl peroxides vs. the azonitrile. Again, the Mn's, MWD's, and solution viscosities were lower using the t-amyl peroxide as compared to the azonitrile. Other performance advantages compared to the azonitrile are illustrated in Table 4. The t-amyl peroxides produce acrylic HSC resins with much lower % total residual monomer and lower APHA color. In most cases, the % total residuals were less than 0.5 % with the use of t-amyl peroxides compared to levels greater than 1 % with the azonitrile. Therefore, polymerizations using an azonitrile in many cases also need a chaser or finishing initiator to reduce residual monomer levels.

In this case, the improvement in molecular weight properties and the lower residual monomer levels are related to the differences in the rate of decomposition or half-life. Because most acrylic HSC polymerizations are conducted at temperatures greater than 100°C and the half-life of the azonitrile is low (15 minute $t_{1/2} = 95^\circ\text{C}$ - Appendix I), the rate of decomposition is very fast and thus the efficiency of the polymerization is reduced. In addition, the APHA color values for all the t-amyl peroxide produced resins were less than 30 compared to the azonitrile produced resins which were greater than 50. The nitrile functionality of the azonitrile initiator can yield by-product compounds that generate color in acrylic resins.

Table 4 Molecular Weight and Viscosity Properties of Acrylic HSC Resins Synthesized with t-Amyl Peroxides vs. AMBN

Initiator	Polym Temp (°C)	Mn	Mw/Mn	Mz/Mn	Viscosity ¹ (poise)	Residual Monomer ²	APHA
DTAP	157	2500	1.81	2.96	15	0.3	27
AMBN	157	2800	2.00	3.61	28	1.2	84

L533	145	2800	2.00	3.62	25	0.4	29
AMBN	145	3400	2.04	3.78	49	1.0	62
L555	134	3300	1.90	3.10	38	0.5	20
AMBN	134	3700	2.04	3.71	50	0.8	74
L531	124	4600	2.41	5.32	93	0.4	20
AMBN	124	4800	2.15	4.03	103	1.2	61
L575	103	6400	2.09	3.73	152	0.8	28
AMBN	103	6600	2.41	4.92	250	1.5	53

- 1 Brookfield viscosity at 260°C and 75% solids content
- 2 Total Residual Monomer

Initiator Combinations

By using initiator combinations of either different half-lives or different chemical structures (e.g., a high energy free-radical generating initiator in combination with a low energy free-radical generating initiator), one can obtain substantial improvements in acrylic HSC resin properties. In the synthesis of acrylic HSC resins, initiator combinations can be a means of further improving the molecular weight and viscosity properties, obtaining a more uniform rate of polymerization, reducing the residual monomer levels, and reducing the polymerization time.

Initiator combinations can be a blend of two initiators that are fed to the reactor simultaneously or can be two initiators that are fed to the reactor sequentially. In this study, acrylic HSC resins were synthesized using 50/50 combinations (based on an active [O] content of 0.21 phm each) of dicumyl peroxide (DCP) and di-t-amyl peroxide (DTAP) in Aromatic 100 solvent at 154°C. The DCP and DTAP have similar 15 minute $t_{1/2}$ temperatures (150°C and 157°C, respectively); however, the types of radicals generated are very different. When DCP decomposes, two cumyloxy radicals or, if β -scission occurs, two methyl radicals are generated. Both the cumyloxy and methyl radicals are high energy radicals and capable of abstracting hydrogens. When DTAP decomposes, one would expect the ethyl radicals to be generated which are lower in energy and with a reduced tendency of abstracting hydrogens and of changing the molecular weight properties of the polymer.

The initiator combinations were studied as blends and in sequential addition, i.e., the sequential addition involved adding DCP to the reactor in the first 2.5 hours of the feed, then DTAP was added in the second 2.5 hours of the feed. Samples of the acrylic HSC resin were removed from the reactor every hour of the feed and analyzed for molecular weight. Table 5 shows the molecular weight averages and polydispersity after each hour of the feed and the final properties after the one hour post-feed reaction.

The molecular weight properties listed in Table 5 show that DTAP yields lower molecular weight at any given time in the polymerization and reduces the increase (or change) in molecular weight and polydispersity over the entire polymerization as compared to DCP. Therefore, it appears that the majority of the molecular weight increase occurs in the later stages of the polymerization when the concentration of the acrylic polymer is high, with an organic peroxide that generates high energy free-radicals like DCP.

The molecular weight properties of the DCP/DTAP combination fall almost exactly between the DCP and DTAP plots and shows a gradual increase in Mw over time. The DCP/DTAP sequential addition is very different, in that, the first 2 hours of the polymerization (where only DCP is being added) is as expected like the DCP alone plot; however, as DTAP is introduced (after 2.5 hours), the molecular weight and polydispersity do not change. Therefore, organic peroxides that yield lower energy free radicals, like t-amyl peroxides, reduce changes in the molecular weight properties that result in higher molecular weight and higher polydispersity.

Table 5 Acrylic HSC Resin Properties Using Initiator Combinations and Sequential Initiator Feeds.

Feed Time	Initiator(s)	Mn	Mw	Mw/Mn
1 st Hour				
	DTAP	2200	3600	1.6
	DCP/DTAP COMB.	2400	4100	1.7
	DCP/DTAP SEQ.	2500	4400	1.7
	DCP/AMBN SEQ.	2600	4500	1.7
	DCP	2500	4500	1.8
2 nd Hour				
	DTAP	2300	4000	1.7
	DCP/DTAP COMB.	2500	4400	1.8
	DCP/DTAP SEQ.	2700	5000	1.9
	DCP/AMBN SEQ.	2600	5100	1.9
	DCP	2700	5000	1.9
3 rd Hour				
	DTAP	2400	4200	1.7
	DCP/DTAP COMB.	2600	4800	1.8
	DCP/DTAP SEQ.	2700	5300	2.0
	DCP/AMBN SEQ.	2700	5300	2.0
	DCP	2900	5600	1.9
4 th Hour				
	DTAP	2500	4500	1.8
	DCP/DTAP COMB.	2700	5500	2.0
	DCP/DTAP SEQ.	2700	5400	2.0
	DCP/AMBN SEQ.	2700	5500	2.0
	DCP	3000	6300	2.1
5 th Hour				
	DTAP	2600	4800	1.8
	DCP/DTAP COMB.	2800	5500	2.0
	DCP/DTAP SEQ.	2700	5500	2.0
	DCP/AMBN SEQ.	2800	5900	2.1
	DCP	3100	6800	2.2
6 th Hour (Final)				
	DTAP	2600	4900	1.9
	DCP/DTAP COMB.	2800	5700	2.0
	DCP/DTAP SEQ.	2700	5600	2.0
	DCP/AMBN SEQ.	2800	6100	2.2
	DCP	3100	7000	2.3

Experimental Design

An experimental design was used to study the effect of polymerization temperature, initiator concentration, and monomer feed rate on the viscosity of acrylic HSC resins. The purpose of using statistically designed experiments is to determine the important variables without the need to prepare a very large series of resins. In this study, the experiments were designed to evaluate the effect of the three variables as they relate to the rate of decomposition or half-life of the initiator on the resin properties. L555 (t-amyl peroxyacetate) was the initiator used in the study.

Two polymerizations of 134°C and 155°C which correspond to half-life times of 15 minutes and 2 minutes, respectively, two initiator concentrations of 3.83 phm and 4.75 phm (by wt., based on parts per hundred monomer, phm), and two feed rates of 3 hours and 5 hours were evaluated. Only 8 polymerizations were needed to study the effects of the three variables. The experimental data, number average molecular weight (Mn), polydispersity (Mw/Mn), and viscosity of 75 % NVM acrylic resins are listed in Table 6.

Table 6 Properties of Acrylic HSC Resins by Statistically Designed Experiments

Temp. (°C)	Conc. ¹ (phm)	Feed (hours)	Mn	Mw/Mn	Viscosity ² (poise)
134	3.83	3	3700	2.06	69.4
134	3.83	5	3600	2.05	61.4
134	4.75	3	3300	2.04	52.0
134	4.75	5	3100	2.04	49.2
155	3.83	3	2900	1.97	36.3
155	3.83	5	2800	1.97	34.0
155	4.75	3	2600	1.88	25.3
155	4.75	5	2500	1.92	23.4

¹ Using t-amyl peroxyacetate

² Brookfield viscosity at 25°C and 75% nonvolatile matter (NVM)

A half normal probability regression analysis was carried out on the three variables vs. viscosity using the statistical computer program Design-Ease.¹⁰ The results of the analysis showed that the primary effect was the polymerization temperature or half-life of the initiator, followed by the initiator concentration. The feed rate showed a minor effect. Therefore, statistically designed experiments are very useful in determining the optimum polymerization conditions for an initiator in order to obtain the desired molecular weight and viscosity properties.

South Florida Outdoor Weathering

Clearcoat acrylic melamine coatings synthesized with L575 and L533 were formulated and applied over white TiO₂ basecoats. The samples were subjected to five years of South Florida outdoor weathering. The study was designed to evaluate the performance of acrylic melamine coatings synthesized with t-amyl peroxides compared to an azonitrile initiator. The control is an automotive OEM clearcoat formulation (PPG Industries). The performance properties shown in Table 7 include 60° gloss, 20° gloss, distinctness of image (DOI), and total color change (delta E).

After five years of South Florida Weathering, the L533 and L575 coatings performed as well as or even better than the commercial control. The L575 and L533 coatings retained higher 20° gloss (69 % and 65 %, respectively) than the commercial control (58 %). The other properties are equivalent in performance to the commercial control.

SUMMARY

The dominant role of the initiator in the synthesis of high solids acrylic coatings resins has been demonstrated. The chemical nature of the initiator, half-life, and the polymerization conditions greatly influenced the molecular weight, MWD, and the solution viscosity of the acrylic resin. The use of t-amyl peroxides and initiator combinations yielded acrylic resins of superior quality over conventional organic peroxides and azonitrile initiators. In addition, statistically designed experiments were useful in determining the important polymerization variables and optimizing the process.

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10. DESIGN-EASE is a Registered Trademark of STAT-EASE, INC., Minneapolis, MN, USA.

TABLE 7 South Florida Weathering Results for Acrylic Melamine Clearcoat Coatings Synthesized with t-Amyl Peroxides Over a White TiO₂ Basecoat After 5 Years Exposure

Property/Years	URC-1000 ¹	L533 ²	L575 ²
60° Gloss			
0	96	96	96
1	94	92	92
2	90	90	91
3	88	90	91
4	83	84	87
5	82	82	84
Retained	85 %	85 %	88 %
20° Gloss			
0	92	89	89
1	84	80	81
2	71	70	74
3	70	73	79
4	59	61	68
5	53	58	61
Retained	58 %	65 %	69 %
DOI			
0	67	45	58
1	59	46	56
2	52	43	51
3	47	39	45
4	40	36	41
5	32	33	29
Retained	48 %	73 %	50 %
Delta E			
1	0.4	0.2	0.9
2	0.5	0.3	1.0
3	0.7	0.4	1.1
4	1.7	0.7	1.6
5	1.8	1.1	1.9

¹ Proprietary Acrylic Melamine Formulation - PPG Industries.

² 75:25 Acrylic:Melamine Ratio (Cymel 303 – Cytec Corporation, formerly American Cyanamid)

Appendix I Initiator Properties

Chemical Name	Code Name	Active [O] ¹ or [N] (%)	Weight % ² (phm)	15 min ³ t _{1/2} (°C)
T-amyl peroxy-2-ethylhexanoate	Lup 575	6.95	6.03	103
T-butyl peroxy-2-ethylhexanoate	Lup 26	7.40	5.67	106
1,1-di-(t-amyl peroxy)cyclohexane	Lup 531	11.11	3.78	124
1,1-di-(t-butyl peroxy)cyclohexane	Lup 331	12.30	3.41	128
T-amyl peroxyacetate	Lup 555	10.96	3.83	134
T-butyl peroxyacetate	Lup 70	12.12	3.46	136
Ethyl 3,3-di(t-amyl peroxy)butyrate	Lup 533	10.00	4.20	145
Ethyl 3,3-di(t-butyl peroxy)butyrate	Lup 233	10.95	3.83	147
Dicumyl peroxide	Lup DCSC	5.92	7.09	150
Di-t-amyl peroxide	Lup DTA	9.19	4.57	156
Di-t-butyl peroxide	Lup DI	10.95	3.83	162
2,2' azobis (methyl butyronitrile)	AMBN	7.29 [N]	5.76	95

¹ At 100% assay

² phm = parts per hundred parts monomer at an active [O] or [N] = 0.42 phm

³ Based on Half-Life software by Arkema Inc. (formerly ATOFINA Chemicals, Inc.)