



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C08K 5/08, C08L 55/02	A1	(11) International Publication Number: WO 88/ 02013 (43) International Publication Date: 24 March 1988 (24.03.88)
(21) International Application Number: PCT/US87/02223 (22) International Filing Date: 3 September 1987 (03.09.87) (31) Priority Application Number: 905,106 (32) Priority Date: 8 September 1986 (08.09.86) (33) Priority Country: US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: YANACEK, James, A. ; 405 Sylvan Lane, Midland, MI 48640 (US). DONALD, Robert, J. ; 2500 Church Point, Midland, MI 48640 (US). MURPHY, Christopher, S. ; 2190 Chalgrove Street, Troy, MI 48098 (US).		(74) Agent: MACLEOD, Rederick, B.; The Dow Chemical Company, The Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: AU, JP, KR. Published <i>With international search report.</i>
(54) Title: COLOR BALANCED RUBBER-REINFORCED PLASTIC		
(57) Abstract <p>A rubber-reinforced polymeric composition having enhanced color stability upon exposure to ultraviolet (UV) light comprising a color balancer in an amount effective to reduce the overall color shift of the plastic due to exposure to UV light.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

COLOR BALANCED RUBBER-REINFORCED PLASTIC

Due to their desirable physical properties such as strength and toughness (i.e., the combination of elongation and impact strength), rubber-reinforced polymer resins are employed in a variety of commercial applications. A deficiency of rubber-reinforced plastic materials made from these resins is their vulnerability to environmental conditions, which causes yellowing of the plastic. In certain applications exposure to a light source having as a component ultraviolet (UV) light, e.g., sunlight or fluorescent lighting, can detract from the appearance of plastic parts by causing discoloration of the resin surface, which is commonly referred to as weathering.

Yellowing of rubber-toughened plastic is particularly critical in markets such as business machine housings and parts. The conversion from metals

20

25

to plastics has resulted in rubber-reinforced plastic components such as business machine housings, which are vulnerable to the degradative effects of fluorescent lighting and sunlight.

5

The UV stability of thermoplastic business machine housings is receiving close scrutiny from suppliers of multiple component personal computer systems. By using a resin having good UV stability, a manufacturer is assured that the housing of any peripheral component, e.g., a printer or additional disc drive, added at a later date will match the color of the housing of the original equipment. Consistent color among different business machine housings gives the consumer a strong perception of quality.

10
15

Interest in UV stability is also being fueled by pressures to make every aspect of business machines as cost effective as possible. In many cases, this is necessitating a switch from the use of structural foam with a highly UV-stable coating to the use of injection molded housings with integral color for equipment housings.

20

25

Before UV can cause any harm, it must first be absorbed. Only certain groups within polymer molecules, called chromophores, accept the energy of the UV light and are transformed into excited state groups. These groups then dispose of the energy. The energy may be transferred to a nearby stabilizer molecule called a quencher, which in turn converts the energy to heat or, less desirably, may break weak chemical bonds with minimal color change.

30

35

-3-

Limited stabilization can be achieved by several conventional mechanisms. UV absorbers operate largely by competitive absorption. Absorbers convert the absorbed energy into harmless heat. Thus, much less light reaches chromophores in the substrate.

An ideal UV absorber should be extremely photo-stable and have high absorption over the entire UV range from 290 to 400 nanometers (nm).

The 2-hydroxyphenyl benzotriazoles are one class of UV absorbers. The benzophenones are another important and widely used class of UV absorbers whose absorption covers mainly the lower half of the UV range. Products of this latter class tend to be more prone to yellowing under processing or light exposure conditions than 2-hydroxyphenyl benzotriazoles. A third class of UV absorbers include rutile TiO₂ metal oxides such as pigment grade titanium dioxide. The benefits of TiO₂ are believed to be more than just as a UV absorber. Higher TiO₂ concentration in a resin increases the sample opacity thereby hindering the observation of discoloration deeper within the material.

Other classes of UV absorbers, which absorb primarily at the low wavelength end of the UV range, include salicylates, cyanoacrylates, benzylidene, malonates, and oxalarrilides. These are generally less effective than UV absorbers in the first three classes.

Hindered amine light stabilizers (HALS) provide another approach to UV stabilization. These molecules, typically derivatives of tetramethylpiperidines, do not absorb UV light, but are effective scavengers of free

radicals, thus acting as photooxidation inhibitors. Synergistic enhancement of stabilizing activity is often achieved by simultaneous use of scavengers and stabilizers, which each act by different mechanisms.

5 When choosing a plastic composition, end users in the past have had to make significant expenditures to achieve ultraviolet light stabilization, or accept an inevitable amount of discoloration. Improved

10 stabilization has been achieved using a combination of TiO_2 and a HALS additive. However, due to the cost of the HALS additive, this stabilization combination entails significant expense.

As previously mentioned, quenchers interact

15 with excited states of chromophores to accept the energy transferred and to return the excited chromophore to the stable ground state. Typical quenchers are nickel chelates which can accept energy

20 from excited chromophores. In addition, some of the protective action of this class has been attributed to their hydroperoxide decomposing and radical scavenging ability.

In view of the problems in achieving color

25 stabilization of rubber-reinforced resins, it remains highly desirable to provide an inexpensive additive for rubber resins which minimizes an overall color shift upon exposure of the resin composition to UV light.

30 The present invention provides a composition comprising a rubber-reinforced plastic containing a flame retardant additive, wherein the composition contains 0.001 to 0.1 weight percent of a yellow color

35 balancer, said color balancer being an organic dye or pigment and being effective to reduce the overall color

shift ΔE of the plastic upon exposure to ultraviolet light.

5 The invention also provides a method of reducing the overall color shift, ΔE , of a rubber-reinforced plastic composition containing a flame retardant additive upon exposure to ultraviolet light, said method comprising incorporating into the composition a fadeable, yellow color balancer, said
10 color balancer being an organic dye or pigment and being present in an amount of 0.001 to 0.1 weight percent.

15 Certain fadeable, yellow organic dyes and pigments have been used to color resins, said dyes and pigments would be used in substantially greater amounts than 0.1 weight percent to color rubber-reinforced plastic compositions.

20 Rubber-containing thermoplastics are well known to those in the art and reference is made thereto for the purposes of this invention. Exemplary resins are those toughened plastics manufactured by bulk solution, bulk-suspension or emulsion polymerization, and thermo-
25 plastics to which rubber has been blended. Representative thermoplastic materials include polymeric resins derived from one or more monovinylidene aromatic compounds such as styrene and, optionally, one or more
30 monomers copolymerizable therewith, such as an ethylenically unsaturated nitrile. Exemplary rubber-reinforced polymers of this type include high impact polystyrene ("HIPS") and ABS type resins.

35 In preparing a copolymer matrix, the amounts of the monovinylidene aromatic compound and comonomer most

advantageously employed will vary depending on the physical and chemical properties desired in the final rubber-reinforced product. In general, the copolymer matrix will advantageously comprise from 5 to 35, preferably 15 to 25 weight percent of the comonomer and from 95 to 65, preferably from 85 to 75 weight percent of the monovinylidene aromatic monomer, said weight percents being based on total polymer weight.

10 Rubbers useful in preparing rubber-reinforced polymer resins are well-known in the art and reference is made thereto for the purposes of the present invention. Advantageously, the rubber employed in preparing said rubber-reinforced product is a homo-
15 polymer or a copolymer of an alkadiene which exhibits a second order transition temperature not higher than 0°C and preferably not higher than -20°C as determined by conventional methods, e.g., ASTM Test Method D-746-52T. A copolymer of ethylene, propylene and optionally, a
20 nonconjugated diene, or an acrylate rubber can also be employed. Preferably, the rubber is a homopolymer of a 1,3-conjugated diene such as butadiene, isoprene, piperylene, chloroprene or a random block or graft
25 copolymer of said conjugated dienes with one or more comonomers. Suitable comonomers include monovinylidene aromatic compounds such as styrene; α -ethylenically unsaturated nitriles such as acrylonitrile; or α -olefins such as ethylene or propylene. Although the
30 rubber may contain a small amount of crosslinking agent, excessive crosslinking can result in the loss of the rubbery characteristics of the rubber.

35 Preferred rubbery polymers are the homopolymers of 1,3-butadiene and block or graft copolymers of at least 55, more preferably from 65 to 85, weight percent

1,3-butadiene, and up to 45, more preferably from 15 to 35, weight percent of a monovinylidene aromatic compound, preferably styrene. The rubber is advantageously employed in an amount such that the rubber-reinforced product contains from 3 to 20 weight percent rubber. A rubber-reinforced product having from 5 to 15 weight percent rubber, based on the total weight of the rubber-reinforced polymer, is preferred.

Techniques suitable for producing the interpolymer of the matrix are well-known in the art. Examples of the known polymerization processes include mass, mass-suspension, mass-solution, suspension, and emulsion polymerization processes as well as other modifications and/or combinations of such processes. See, for example, U.S. Patents 3,509,237; 3,928,494; 4,221,883; 4,239,863; 4,243,765; and 4,250,271.

The bulk and emulsion polymerization processes used for incorporating rubbers into styrene-based polymers are not easily adapted for incorporating rubbers into other polymer systems. Direct blending of a rubber with a thermoplastic polymer is another method for incorporating rubbers into thermoplastic polymers. The standard practice is to prepare the resin separately and to add the rubber later. Additionally, grafted rubber concentrate (GRC), i.e., agglomerated particles of emulsion graft polymerized rubbers, may be compounded with bulk and emulsion prepared compositions and utilized as an impact modifier.

For example, polyvinyl chloride (PVC) may be blended with poly(butadiene-co-acrylonitrile), chlorinated polyethylene, grafted ethylene-vinyl acetate (EVA) copolymer, and grafted ethylene-propylene

rubber (EPR). Ethylene-propylene diene monomer (EPDM) and EPR can be mechanically blended with polypropylene. Toughening agents may also be made by making a masterbatch of rubber and grafted thermoplastic
5 terpolymer such as acrylonitrile-butadiene-styrene (ABS) or methacrylatebutadiene-styrene (MBS).

Plastic materials can be modified by a variety of substances (flame retardant (FR) additives) designed
10 to inhibit ignition or burning characteristics to conform to prescribed standards. This is especially significant in business machine housings. Applicants have found several FR additives add to the
15 discoloration of rubber toughened plastics upon exposure to light having as a component ultraviolet light.

FR additives may interrupt or inhibit one or more of the mechanisms of burning or smoke generation.
20 Some are present as fillers while reactive varieties are introduced into the resin system by chemical reaction. They act by reducing the amount of combustible materials in the product or by interfering
25 chemically with the combustion process either in the vapor or condensed phases.

Among the more common additive-type flame retardants are the halogenated aliphatics, brominated
30 aromatics, halogenated and nonhalogenated organophosphates, and the oxides of aluminum and antimony.

Brominated aromatic compounds are commonly used
35 FR additives for many thermoplastic resins, especially styrenics and polyesters.

Applicants have found that a number of commonly incorporated FR additives increase discoloration of the rubber toughened plastics upon exposure to ultraviolet light. Exemplary of these FR additives are
5 decabromodiphenyl ether, bis(tetrabromophthalimido)-ethane, poly(dibromophenylene oxide), tribromophenoxy-ethane and 1,2-bis(pentabromophenoxy) ethane.

Antimony oxide is unique in that its only value
10 as a flame retardant is in combination with halogen compounds as a synergist. A preferred FR additive comprises 1,2-bis(pentabromophenoxy) ethane and antimony trioxide.

15 Included in the broad category of FR additives are smoke suppressants. Examples are oxides of boron and molybdenum which are commonly incorporated in PVC.

By "color balancers" is meant any yellow
20 organic dye or yellow organic pigment that will fade upon exposure to light having as a component ultraviolet light. The color balancer may be added to the resin as part of a pre-matched color system or as part of the initial color system. The color balancer
25 may be incorporated into the resin in any conventional manner known to those skilled in the art. Exemplary of such techniques is to mix the resin and the color balancer in an extruder.

30 The color balancer chosen should be evaluated on the basis of the UV stability of the end product. It does not make lightfast the rubber-reinforced plastic. Rather, the initial yellow of the color
35 balancer fades to generally compensate for the yellowing of the rubber toughened plastic. Consequently, the

-10-

plastic is not made UV stable, but its overall color shift will be greatly reduced because of the presence of color balancer. The relative amount of color balancer, e.g., dye or pigment, will be dependent on a variety of factors. Such factors include the stability of the dye; the amount of rubber and FR additive in the plastic; and whether the color balancer is included in the initial custom color package, which requires a higher weight percentage than if added to a "pre-matched" system.

Although any yellow organic dye which fades upon exposure to UV light is a suitable color balancer, anthraquinone dyes have now been found to balance resins very well. Anthraquinone dyes are inherently UV unstable, gradually losing yellow intensity upon exposure.

Exemplary anthraquinone dyes are Yellow AGB obtainable from Amoplast Co., and Soluaperm Yellow Gand Solvent Yellow 77 obtainable from the Ferro Compounding Co. A particularly preferred color balancer, 1,8-bis(phenylthio)anthraquinone, is obtainable as Yellow GHS from the Amoplast Chemical Co.

Another particularly preferred color balancer is Macroflex Fl. Y. 10GN, a cumarin dye, obtainable from the Mobay Chemical Company.

Organic dyes may be present in an amount of from 0.001 to 0.04, preferably from 0.001 to 0.02 weight percent of the rubber-toughened plastic.

Also, suitable as color balancers are yellow organic pigments. Unlike dyes, pigments are generally

insoluble and impart color by dispersing throughout the system.

5 Selection of a pigment should be based on properties known to those in the art. Exemplary of such properties are UV stability, hue, tinting strength, hiding power and melt flow. One suitable organic pigment is Fanchon Yellow, obtainable from the Mobay Chemical Company.

10 Organic pigments usually will be present in an amount of from 0.001 to 0.1; preferably from 0.001 to 0.05; and most preferably from 0.03 to 0.05 weight percent of the rubber-toughened plastic.

15 Liquid colorants are dispersions of pigments in a carrier matrix. Carriers for liquid colorants are blends of surfactants, plasticizers, and other ingredients. Migration or bleed is a function of the pigment showing varying degrees of solubility in the plastic or other substance in contact with the colored plastic. Higher-molecular-weight pigments minimize migration problems.

25 For the purposes of this invention, a suitable color concentrate is a composition containing a predetermined percent by weight of color balancer, i.e., organic dye or pigment properly dispersed in a carrier resin. The carrier resin is then blended into
30 a letdown resin, which is colored or modified. The amount of color balancer incorporated into a concentrate can vary greatly, reaching as high as 80 percent or more. The weight of color balancer used per
35 weight of letdown resin is called the letdown ratio, which is expressed as unit weight of letdown resin to

unit weight of concentrate. Although letdown ratios as high as 200:1 are possible, the best color uniformity is obtained with lower ratios, approximately 50:1 or less.

5

Color concentrates usually are mixed with the letdown resin by gravimetric proportional feeders at the extruder hopper. Since the letdown ratio is calculated upon a percent-by-weight basis, the same method must be used to determine the proportion of concentrate and natural resin in the mix. In this way, color uniformity will be assured from run to run.

To determine the proper letdown ratio by percent of color balancer in the mix, the following formula is used:

20

25

30

35

$$5 \quad \left[\frac{\% \text{ Color balancer/in Concentrate } -1}{\% \text{ Color balancer/in Final Part}} \right] : 1$$

10 The carrier resin contained in the concentrate should be generally the same as or compatible with the letdown resin at the letdown ratios employed. Testing prior to actual application will help determine whether changes in the physical properties of the final product will occur. In general, it is most effective to have a
15 homogeneous distribution of color balancer; this is accomplished by a carrier resin with a melting point slightly lower than the melting point of the letdown resin.

20 The color balancer may be added singly or in combination with commonly incorporated UV stabilizers. A particularly preferred combination is to incorporate a color balancer and up to 10 percent by weight of TiO_2
25 in the rubber toughened plastic.

Color shift is the discoloration or change in hue of a plastic exposed to UV radiation. Color shift can be measured by a color variation parameter, delta E
30 (ΔE). Essentially this parameter is a measure of the color difference between an experimental sample and a control sample of the same formulation. Hunter color scales for grayness (L), red/green (a), and yellow/blue (b) are described by K. S. Hunter in "Photoelectric
35 Color Difference", Journal of the Optical Society of America, JOSAA, Vol. 12, No. 12, December, 1958,

-14-

pp. 985-995. Delta E, the total color variation, is calculated by the following formula:

$$\Delta E = (L-L_0)^2 + (a-a_0)^2 + (b-b_0)^2$$

5 where L, a, and b are the color values of the UV exposed experimental sample and L₀, a₀, and b₀ are color values of an unexposed control sample stored in a dark environment, creating initial delta values of zero. Lower ΔE values mean less variation from the control sample values and less discoloration.

10

Delta E, however, gives no indication as to how the color is shifting. Therefore, additional parameters for measuring color change include L, a or b versus exposure time.

15

Weatherometers subject samples to accelerated weathering conditions. Various weatherometers are commercially available to evaluate the ultraviolet stability of rubber-reinforced plastics as measured by ΔE.

20

One suitable weatherometer is the Xenon Arc Ci65 Weatherometer (Xenon Arc), available from the Atlas Electrical Devices Company. This weatherometer utilizes a boro-silicate inner filter and a soda lime glass outer filter; an irradiance output of 0.35 watts per square meter; and a temperature of 55°C. Subjecting a plastic resin to an exposure time of 300 hours at a continual 1.0 revolutions per minute (RPM) in the Xenon Arc Ci65 Weatherometer is designed to simulate approximately 5-7 years of "typical indoor UV exposure". An exposure time of 100 hours is often sufficient to test the commercial acceptability of rubber-reinforced plastic compositions. Preferably,

25

30

35

-15-

the compositions of the invention have an overall color shift of less than 2.0 ΔE after 100 hours and advantageously less than 1.0 ΔE after 300 hours.

5 Another suitable weatherometer is the HPUV Indoor Actinic Exposure System (HPUV), also available from the Atlas Electric Devices Company. This weatherometer utilizes eleven 1500 MA cool white fluorescent lamps and two filtered 430 MA fluorescent
10 sunlamps. Subjecting a plastic resin to an exposure time of 300-400 hours in the HPUV Indoor Actinic Exposure System is designed to simulate 3-5 years of "typical" indoor UV exposure. An exposure time of 100
15 hours in the HPUV Actinic Exposure System is often sufficient to test the commercial acceptability of rubber-reinforced plastic compositions. Preferably, the compositions of the invention have an overall color shift of less than 2.0 ΔE after 100 hours and
20 advantageously less than 1.0 ΔE after 300 hours.

Because of the different weathering methods used in weatherometers, e.g., the Xenon Arc as compared with the HPUV, assessment of the UV stability of a
25 rubber-reinforced plastic is highly dependent on the type of weatherometer utilized. An acceptable delta E recorded in one weatherometer does not ensure a similarly acceptable delta E being recorded in a weatherometer employing a different weathering method.

30 The following examples are presented for the purpose of illustration only. The features and advantages of the present invention are not limited to these examples. All parts and percentages are by
35 weight unless otherwise indicated.

Examples 1-4

An ABS resin prepared by mass polymerization is available as 342EZ[®] (Trademark of The Dow Chemical Company) from The Dow Chemical Company. 342EZ is 56.5 percent of the rubber-modified plastic comprising a continuous polymer phase consisting of 68.75 percent styrene, and 20.5 percent acrylonitrile; dispersed throughout the polymer matrix is polybutadiene in an amount of 9.25 percent.

By emulsion polymerization, a grafted rubber concentrate (GRC) is prepared having a composition of 41.6 percent styrene, 41.0 percent butadiene, 16.7 acrylonitrile. The GRC, used as an impact modifier, comprises 5 percent of the rubber-modified plastic.

A colorant, sold under the tradename of IBM Pearl White by the Ferro Compounding Co., is incorporated in the composition. The colorant is 4.8 percent of the composition, and it was let down at a 20:1 ratio.

Titanium dioxide is added to composition in a 6 percent concentration.

With the ABS, GRC, and colorant are mixed and melt blended the following additives: chlorinated polyethylene fire-resistant additive and synergist, additional stabilizers and lubricants.

Various concentrations of a color balancer, Yellow GHS, is melt blended in an 8.8 twin extruder. The color balancer is added after the color concentrate. A double pass, with tumble blending prior to both the initial and final pass, is utilized to

enhance dispersion. A temperature profile of 165°C at the feed end and 204°C at the dye end is utilized.

5 Pelletized formulations are dried for two hours at approximately 165°C prior to sample molding. 2 x 3.5 x 0.11 inch (5 x 8.9 x 0.28 cm) plaques are molded on a Negri-Bossi injection molder. The barrel temperature profile used is 210°C at the feed end and 218°C at the dye end.

10 Moldings having various levels of Yellow GHS are evaluated for color variation using a reflectance spectrophotometer and the aforementioned Hunter color scales.

15 Early in the test, an initial bleaching of the sample is ordinarily observed (shown by a negative ΔB). After this phenomena, the sample yellowing begins. Delta E is used to monitor the overall color shift.
20 Further, since the main discoloration resulting from UV exposure is in the yellow hue, or the blue/yellow scale, ΔB is monitored. Finally, yellowing is found to occur quite linearly with time, therefore, slopes of ΔB versus time (following the initial bleaching) were
25 measured for comparison of various systems' behavior.

The results of the color variation parameter for moldings of various percent GHS based on the total weight of material are set forth in Table 1.
30

35

TABLE I

Example	Xenon Arc (1)				HPUV (2)			
	%GHS	Final ΔE	Final ΔB	ΔB/100 Hrs	Final ΔE	Final ΔB	ΔB/100 Hrs	
1	0%	1.57/1.46	1.49	0.60/0.65	0.89	0.85	0.32	
2	0.01	0.37/0.42	0.30/0.33	0.32/0.35	0.14	0.09	0.14	
3	0.02	0.72/0.69	-0.71/-0.68	----	0.65	-0.62	-0.12	
4	0.04	2.29/2.29	-2.24/-2.24	----	1.81	-1.75	-0.50	

(1) Samples of rubber-reinforced plastic with varying concentration of color balancer are weathered using a Xenon Arc Ci65 Weatherometer available from the Atlas Electric Devices Company. This instrument utilizes a boro-silcane inner filter and a soda lime glass outer filter; an irradiance output of 0.30 watts per square meter; and a temperature of 55°C. While being rotated in the instrument at 1 revolution per minute (rpm), samples are weathered for 300 hours, which simulates 3-5 years of UV exposure in an actual office environment.

(2) Samples of rubber-reinforced plastic with varying concentration of color balancer are weathered using a HPUV Indoor Actinic Exposure System, available from the Atlas Electric Devices Company. This instrument utilizes 11 1,500 MA cool white fluorescent lamps and two filtered 430 MA fluorescent sunlamps. Depending on the intensity or age of the lamps, samples are 300-400 hours, which simulates 3-5 years of UV in an actual office environment.

As seen by the results in Table I, improved weathering as determined by ΔE and ΔB is achieved by the color balancer, in the form of a yellow organic dye, in an amount below 0.04 percent.

5

Examples 5-7

10

Using the techniques of Example 1, an identical fire-retardant, colored, rubber-modified plastic material is prepared, except that Applicants employed various concentrations of NCR Gray concentrate, a colorant obtained from the Reed Chemical Company.

15

20

25

30

35

TABLE II

<u>Xenon Arc (1)</u>		<u>HPUV (2)</u>					
<u>Example</u>	<u>%GHS</u>	<u>Final ΔE</u>	<u>Final ΔB</u>	<u>ΔB/100 Hrs</u>	<u>Final ΔE</u>	<u>Final ΔB</u>	<u>ΔB/100 Hrs</u>
5	0%	1.24/1.21	1.15/1.13	0.61/0.60	1.37	1.28	0.61
6	0.002	0.80/0.83	0.72/0.75	0.45/0.46	1.06	0.98	0.49
7	0.01	0.34/0.41	-0.31/-0.38	0.26/0.26	0.26	0.17	-0.31

(1) Same as Footnote 1 in Table I.

(2) Same as Footnote 2 in Table I.

As seen by the results in Table II, improved weathering as determined by ΔE and ΔB is achieved by the addition of a color balancer, in accordance with the teachings of this invention.

5

Examples 8-10

Using the technique of Example 1, an identical fire-retardant, colored rubber-modified plastic material is prepared except that Applicants employed various concentrations of IBM Shell Gray concentrate, a colorant obtained from the Ferro Compounding Company.

10

TABLE III

15

Xenon Arc (1)

<u>Example</u>	<u>% GHS</u>	<u>Final ΔE</u>	<u>Final ΔB</u>	<u>$\Delta B/100$ Hrs</u>
8	0%	0.77/0.83	0.76/0.81	0.25/0.27
20 9	0.005	0.44/0.44	0.42/0.41	0.15/0.16
10	0.015	0.33/0.30	-0.23/-0.16	0.00/0.04

(1) Same as Footnote 1 in Table I.

As seen by the results in Table III, improved weathering as determined by ΔE and ΔB is achieved by the addition of a color balancer in accordance with the teachings of this invention.

25

30

Examples 11-12

Using the techniques of Example 1, an identical fire-retardant, colored, rubber-modified plastic is prepared except that Applicants employed, in the original dry blend color match, various concentrations of IBM Pearl White, a colorant available from the Reed Chemical Company.

35

TABLE IV

Example	%GHS	Xenon Arc (1)			HPUV (2)		
		Final ΔE	Final ΔB	ΔB/100 Hrs	Final ΔE	Final ΔB	ΔB/100 Hrs
11	0%	1.03/1.09	0.98/1.04	0.42/0.45	1.26	1.20	0.44
12	0.01	0.66/0.60	0.63/0.57	0.32/0.29	1.07	1.03	0.39

(1) Same as Footnote 1 in Table I.

(2) Same as Footnote 2 in Table I.

As seen by the results in Table IV, improved weathering as determined by ΔE and ΔB is achieved by the addition of a color balancer, a yellow organic dye, in the original color package.

5

10

15

20

25

30

35

CLAIMS

1. A composition comprising a rubber-reinforced plastic composition containing a flame retardant additive, wherein the composition contains
5 0.001 to 0.1 weight percent of a fadeable, yellow color balancer, said color balancer being an organic dye or pigment and being effective to reduce the overall color shift, ΔE , of the composition upon exposure to
10 ultraviolet light.
2. A composition as claimed in Claim 1, wherein the overall color shift of the rubber-reinforced plastic will be less than 2.0 ΔE after being
15 subjected to accelerated weathering conditions for 100 hours at 55°C in a Xenon Arc Ci65 Weatherometer, and/or accelerated weathering conditions for 100 hours in a HPUV Indoor Actinic Exposure System.
- 20 3. A composition as claimed in Claim 1, wherein the overall color shift of the rubber-reinforced plastic will be less than 1.0 ΔE after being

subjected to accelerated weathering conditions for 300 hours at 55°C in a Xenon Arc Ci65 Weatherometer and/or accelerated weathering conditions for 300 hours in a HPUV Indoor Actinic Exposure System.

5

4. A composition as claimed in Claim 1, wherein the color balancer is an organic dye present in an amount of from 0.001 weight percent to 0.02 weight percent.

10

5. A composition as claimed in Claim 1, wherein the color balancer is an anthraquinone dye.

15

6. A composition as claimed in Claim 5, wherein the anthraquinone dye is 1,8-bis(phenylthio)-anthraquinone.

20

7. A composition as claimed in Claim 1, wherein the color balancer is an organic pigment present in an amount of from 0.001 weight percent to 0.05 weight percent.

25

8. A composition as claimed in Claim 7, wherein the organic pigment is present in an amount of from 0.03 weight percent to 0.05 weight percent.

30

9. A composition as claimed in Claim 1, further comprising a pigment grade TiO_2 in an amount of up to 10 weight percent.

35

10. A composition as claimed in Claim 1, wherein the flame retardant additive is 1,2-bis(pentabromophenoxy)ethane and antimony trioxide.

11. A composition as claimed in Claim 1, further comprising a colorant different from the color balancer.

5 12. A method of reducing the overall color shift, ΔE , of a rubber-reinforced plastic composition containing a flame retardant additive upon exposure to ultraviolet light, said method comprising incorporating into the composition a fadeable, yellow color balancer, 10 said color balancer being an organic dye or pigment and being present in an amount of from 0.001 to 0.1 weight percent.

15 13. A method as claimed in Claim 12, wherein the color balancer is added to the composition as part of a pre-match color system or as part of an initial color system.

20

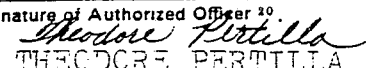
25

30

35

INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/02223

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC 4; CC8K 5/08; CC8L 55/02 U.S. CL. 524/358, 504; 525/86		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System ¹	Classification Symbols	
U.S.	524/110, 358, 469, 504, 505; 525/86	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁵	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US, A, 3,441,536 PUBLISHED 29 APRIL 1969, see column 2, lines 1 to 25; column 3, lines 32 to 75; column 4, lines 8 to 65, CHI K. DIEN.	1-13
A	US, A, 3,494,982 PUBLISHED 10 FEBRUARY 1970, see column 4, lines 47 to 58, GRABOWSKI ET AL.	1-13
A	US, A, 3,172,872 PUBLISHED 09 MARCH 1965, see column 1, lines 15 to 64; column 2, line 12; column 3, lines 51 to 57, KRAUS ET AL.	1-13
<p>¹⁵ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²	Date of Mailing of this International Search Report ³	
16 OCTOBER 1987	03 NOV 1987	
International Searching Authority ¹	Signature of Authorized Officer ²⁰	
ISA/US	 THEODORE PERTILLA	