Colorants Based on Renewable Resources and Food-Grade Colorants for Application in Thermoplastics

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ABSTRACT: A series of colorants based on renewable resources and food-grade colorants have been evaluated for use in polypropylene (PP) and polyvinylchloride (PVC). It has been found that most of these colorants can be processed in PP at 200°C or even 260°C while maintaining good color intensity and color brightness. The colorants evaluated cover a large part of the color spectrum. In PP, the light stability of alizarin (red), carmine (red), indigo (blue), purpurin (red), quinizarin (red), and the aluminium lakes of quinoline yellow (yellow) and indigo carmine (blue) is close to the requirements for indoor applications. The blue colorants indigo and the aluminium lake of indigo carmine are, in principle, sufficiently light stable in PP for indoor applications. A few colorants showed bleeding from PP. Bonding of migrating colorants to the reactive carrier maleic anhydride grafted polypropylene, however, reduced bleeding of the colorant to a large extent. Also after processing in PVC at 200°C, good color intensity and saturation is maintained. Quinizarin, a structural analog of alizarin and purpurin, shows a light stability performance that is close to commercial lead chromate/molybdate orange based colorants. The best performing natural colorants are sufficiently heat and light stable for applications where moderate properties concerning heat resistance and (UV) light stability are required, such as underground PVC water drainage pipes and indoor PP applications. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2961–2969, 2004

Key words: renewable resources; dyes/pigments; thermoplastics; thermal properties

INTRODUCTION

Trends in colorants

During the 20th century, cadmium, lead, and chromium have provided a widely used low-cost base for colorants with a good performance. Increasing awareness for human health and environmental concern, however, has led to the striding ban of these heavy metal-based colorants in all kinds of materials and products. In Sweden and Switzerland, the use of cadmium-based colorants in plastics is prohibited already since 1981 and 1987, respectively, and the alleged toxic character of cadmium has led to the marketing of alternatives for cadmium-based colorants from the early 1980s.[1,2] Since the late 1980s, legislation in Western Europe and the United States is directed towards an ever broadening ban of lead, chromium, mercury, and in particular, cadmium. In plastics, lead chromate/molybdate-based colorants are currently gradually being replaced by nonheavy metal inorganic and organic colorants.[3–6] Alternative inorganic colorants, however, often fail to impart the desired brilliance to products,[6–8] whereas organic colorants are being produced with the use of elaborate chemistry, frequently making use of highly reactive intermediates but not seldom making use of suspected human carcinogens like 3,3-dichlorobenzidine,[9] giving the need for extensive health and hazard considerations during production. Natural and/or edible colorants might offer an interesting alternative to the currently used inorganic or organic colorants.

Natural colorants for use in plastics

Natural colorants and derivatives are, besides used as colorants for food, used and studied in various applications such as antioxidants, textiles, inhibitors for medical therapy, promotors for light-induced photooxidation of pesticides contaminating surface water, insecticides against the carpet beetle.[10–17] The potential application of natural colorants in plastics is, however, as far as known by the authors, hardly addressed in the literature until now.

In the literature, natural colorants for food applications and dyeing of textiles are often described as heat and light sensitive.[18,19] On the other hand, good lightfastness and heat stability performance is reported for natural colorants like alizarin, carminic acid, carmine,

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TABLE I
Natural and Synthetic Food-Approved Colorants Mixed in PP, Including Their E-Number if Food Approved in the EU, Their Color and Origin and the Supplier of the Colorants Used in This Research

Colorant	E-number	Color	Origin	Supplier
Alkannin		Blue	Root of *Alkanna tinctoria*	Livos[a]
Alizarin (97%)		Yellow (brownish)	*Rubia tinctorum*	Acros
Amaranth, Al lake	E123	Purple	Synthetic	W-J[a]
Brilliant Blue FCF, Al lake	E133	Blue	Synthetic	W-J
Carmine	E120	Red	Aluminium lake of carminic acid	Acros
Carminic acid (96%)	E120	Red	Cocheneal insect (*Coccus Cacti* L.)	Acros
Carmoisine, Al lake	E122	Red	Synthetic	W-J
Catechin		Brown	Wood of Acacia	Livos
Chlorophyllin	E140	Green (greyish)	Chlorofyll (Leaves of tree)	W-J
Copper chlorophyllin YS	E141	Green	Chlorofyll (Leaves of tree)	W-J
Curcumin (98%)	E100	Yellow	Roots of *Curcuma longa* and *C. domestica*	Acros
Cyanidine-3-glucoside		Yellow	Rind of oranges	ATO
Erythrosine, Al lake	E127	Pink	Synthetic	W-J
Henna (99%)		Yellow	Leaves of *Lawsonia inermis* and *L. alba*	Acros
Indigo		Blue	Woad (*Isatis tinctoria*)	Acros
Indigo carmine	E132	Blue	*Indigofera tinctoria*	Acros
Indigo carmine, Al lake	E132	Blue	Synthetic	W-J
Juglone		Brown	Walnut shell	Livos
Luteolin		Yellow	Weld plant (*Reseda luteola*)	Livos
Morin + maclurin + kampferol		Brown	Wood of Mulberry tree	Livos
Patent Blue V, Al lake	E131	Blue	Synthetic	W-J
Phycobiliproteins		Purple	Algae (*Porphyridium* sp.)	IAB[a]
Phycobiliproteins		Pink	Algae (*Porphyridium* sp.)	IAB
Ponceau 4R, Al lake	E124	Red	Synthetic	W-J
Purpurin		Red (brownish)	*Rubia tinctorum*	Acros
Quinoline Yellow, Al lake	E104	Yellow	Synthetic	W-J
Riboflavin (98%)	E101	Yellow	A.o. from yeast (Vitamin B2)	Acros
Rubropunctatine		Red	Monascus fungi	ATO
Sunset Yellow, Al lake	E110	Orange	Synthetic	W-J
Tartrazine, Al lake	E102	Yellow	Synthetic	W-J

[a] Livos = Livos Pflanzenchemie. W-J = Warner Jenkinson Europe. IAB = Institute for Applied Bioscience of the Ben Gurion University, Israel.

indigo, annatto, and curcumin in applications like textiles, maxillofacial prostheses, and food.[19–23] This good to excellent heat and light stability reported for textile and food applications, however, does not automatically implicate an excellent performance in plastics. It, nevertheless, forms an encouraging starting point to study their behavior in thermoplastic materials.

Aim of this study

This study investigates the possibilities of using natural colorants of plant, fungal, and algae origin as well as synthetic food-approved colorants of mainly organic nature in the thermoplastic polymers polypropylene (PP) and polyvinylchloride (PVC). The colorants are processed at the usual thermoplastic processing temperatures, and evaluated with respect to color, bleeding, and temperature and (UV) light stability. The performance of the natural colorants will be compared to those of commercially available colorants like the widely applied lead chromate PY 34 and the recently developed cerium sulphide colorant PO 78.

EXPERIMENTAL

Materials

An overview of the natural and synthetic food grade colorants tested in this study is given in Table I. For all colorants used in this research, their color, origin, and supplier are summarized. Additionally, the so-called E-number of the food-approved colorants in the EU is given. The colorants obtained from Livos were extracts from plant tissue and of technical purity.

Cyanidine-3-glucoside was extracted from the rind of oranges by refluxing in ethanol for 2 h. The yellow colorant was isolated by vacuum evaporation at 40°C and 35 mmHg.

Red Monascus colorants were produced by submerged fermentation with Monascus ruber.[24]

All colorants were in powder form, except for the colorant from the walnut shell, juglone, which was a sticky material.

Inorganic and synthetic organic colorants tested in this research are summarized in Table II, together with

TABLE II
Inorganic and Synthetic Organic Colorants Mixed in PP, Their C.I. Color Number, Color, Trade Name, and Supplier of the Colorants Used in This Research

Colorant	C.I. number	Color	Trade name	Supplier
Chromium titanate	PBr 24	Yellow	Irgacolour 10415	Cerdec
Nickel titanate	PY 53	Yellow	Lichtgelb 8G	Bayer
Cerium sulphide–Lanthanum sulphide	PO 78	Orange	Neolor Light Orange S	Rhodia
Lead sulphochromate	PY 34	Yellow	Hornachrome Yellow GMXAH-15	Ciba
Benzimidazolone	PY 180	Yellow	PV Fast Yellow HG	Clariant
Anthraquinone	PR 177	Red	Chromophtal Red A3B	Ciba
Indanthrone	PB 60	Blue	Chromophtal Blue A3R	Ciba

their C.I. number, trade name, and the supplier of the samples.

PP was Borealis Borstar HF 136MO, provided by Curver Color Masters, The Netherlands.

Two PVC compounds were provided by Wavin Marketing & Technology, The Netherlands. One PVC compound consisted of PVC (Shin Etsu, grade 6704, 100 phr), calcium carbonate (2 phr), and a one pack lead stabilizer (Allstab). The second PVC compound consisted of PVC (Shin Etsu, grade 6704, 100 phr), calcium carbonate (2 phr), and a heavy metal free new generation organic stabilizer (Crompton).

Methods

Processing of colorants in PP

Batches of 0.2 g of the colorants from Tables I and II and 200 g of PP were kneaded in a Haake Polylab kneader for 10 min at 185°C. The kneader was provided with a Rheomix 3000 unit having a volume of 310 cm^3 and counterrotating roller blades. The turning speed was 100 rpm. The resulting colored PP samples were granulated and injection molded to "falling dart" samples of dimensions 60 × 60 × 2 mm at 200°C using a Demag D25-80 injection-molding machine.

Besides the aluminium lakes of the synthetic food-approved colorants, the more common sodium lakes were identically processed to "falling dart" samples. In addition, the colorants alizarin, indigo carmine, and the aluminium lake of quinoline yellow were injection molded at 260°C.

Lightfastness after accelerated suntest

The colored PP samples were irradiated in a Heraeus Suntest CPS for 48 h at maximum power, being 765 W/m^2. Before and after irradiation, the L,a,b-color values were determined according to the CIE-lab standard using a Dr. Lange Spectropen and the change in color, expressed as ΔE, was determined. During measuring of the L,a,b-values, a couple of sheets of white printing paper were placed below the colored PP samples. UV-VIS spectra of the aluminium lakes of quinoline yellow and brilliant blue FCF in PP, before and after 48 h of Suntest irradiation, were determined as well.

Migration of colorants from PP

Colored PP samples, 10 × 10 × 2 mm, were put in 5 mL of a series of solvents in the dark during 10 and 60 days, respectively. The solvents were water, neutral, acidic (pH = 2.6), as well as alkaline (pH = 10), ethanol, sunflower oil, and hexane. After removal of the PP samples, the solvents were analyzed using UV-VIS. As a reference, the clean solvent and solutions of known concentrations of the colorants in the respective solvents were analyzed.

Processing of colorants in PVC

Batches of 0.12 g of the colorants from Tables VII and VIII and 120 g of PVC, both heavy metal-free (HMF)-stabilized as well as lead (Pb)-stabilized PVC, were processed on a Schwabenthan two-roll mill for 3 min at 195–200°C. After 3 min mixing, the colored PVC samples were taken from the two-roll mill in the form of sheets.

RESULTS AND DISCUSSION

Processing in PP

The majority of the natural and synthetic food grade colorants presented in Table I yielded homogeneous dispersion and good coloration in PP after kneading and subsequent injection molding at 200°C. Exceptions are the acacia (catechine) and weld (luteoline)-based colorants and indigo carmine, all three showing very small speckles in the PP samples. The yellow colorants curcumin and henna turned orange upon dispersion in PP, the yellow alizarin turned red. This change in color is probably due to interaction with metal ions or deprotonation of the colorants.[25] The green chlorophyllin colorants and luteolin give off a smell during processing.

TABLE III
Color, L, a, b-Values, and Lightfastness after 48 h Irradiation in a Suntest of Natural and Synthetic Food-Approved Colorants, 0.1 wt % Mixed in PP

Colorant	Color in PP	L	a	b	ΔE in PP
Indigo carmine	Blue[a]	37	−12	−14	2.3
Purpurin	Red	16	25	20	2.6
Alizarin	Red	13	17	14	4.2
Indigo	Blue	4.5	4.2	−3.9	4.3
Quinoline Yellow, Al lake	Yellow	71	−2.6	66	4.9
Indigo carmine, Al lake	Blue	49	−12	−22	6.2
Carmine	Purple (reddish)	33	43	12	7.7
Riboflavin	Yellow	54	16	67	10
Carminic acid	Purple (reddish)	18	29	15	12
Copper chlorophyllin YS	Green	42	−16	31	14
Amaranth, Al lake	Purple	34	41	2.3	18
Chlorophyllin	Green	44	0.2	40	23
Henna	Orange	48	36	58	28
Curcumin	Orange	34	34	39	35
Tartrazine, Al lake	Yellow	69	9.8	76	35
Brilliant Blue FCF, Al lake	Blue	45	−32	−30	38
Sunset Yellow, Al lake	Orange	58	35	62	45
Ponceau 4R, Al lake	Red (pinkish)	48	45	30	48
Carmoisine, Al lake	Red (pinkish)	37	48	23	52
Erythrosine, Al lake	Pink	51	56	4.0	52
Alkannine	Blue	11	6.4	−7.2	58
Patent Blue V, Al lake	Blue	41	−28	−33	60

[a] Poor dispersion.

The colored PP samples cover a large part of the color spectrum. The color and L,a,b-values of the colored PP samples are given in Table III. In general, the PP samples have a pure and bright color, as can be concluded from the high chroma values a and b. The color strength of most colorants is good, with exceptions for catechine, cyanidine-3-glucoside, juglone, luteolin, phycobiliproteins, rubropunctatine, and morin and maclurin. In fact, the color of the latter colorants has faded nearly completely. This may be related to excessive thermal degradation or to limited purity of the colorants actually being extractives from plant tissues or of algal or fungal origin. Because of the pale color of these samples, the L,a,b-color values are not presented in Table III. Indigo carmine yields moderate color strength after processing in PP, and alizarin and indigo show an excellent color strength. These data prove that most of the investigated colorants have a good to excellent thermostability in PP and can endure temperatures as high as 180–200°C for at least 10 min. The colorants alizarin and the aluminium lakes of indigo carmine and quinoline yellow have even been injection molded at 260°C with preservation of the color.

The colored PP samples are translucent, indicating that the colorants are either dissolved in PP or well-dispersed particles, having sizes well below the wavelength of visible light, 400 nm. According to Swank, well-dispersed particles will yield clear and translucent samples when sizes are below 50 nm.[26] Addition of small amounts of TiO_2 resulted in nice opaque-colored PP samples.

Contrary to the aluminium lakes of the synthetic food-approved colorants, the sodium salts yield a poor dispersion and, probably as a consequence of it, a poor color strength.

A number of commercially applied colorants have been tested as a reference (Table IV). The titanate pigments PBr24 and PY53 are selected for being food contact-approved and because they are experienced by Curver Color Masters (The Netherlands) to have a good color strength and excellent light stability at a low price, €2.5–5 kg vs. €25–50 for many organic colorants. These titanate pigments result in opaque samples with moderate color strength. The known excellent light stability of the titanate pigments is not found under the experimental conditions used. The cerium-based pigment PO78 is selected for being a recent development in the spectrum of heavy metal-free inorganic colorants. It gives a translucent sample in PP

TABLE IV
Color, L, a, b-Values, and Lightfastness after 48 h Irradiation in a Suntest of Inorganic and Synthetic Organic Colorants, 0.1 wt % Mixed in PP

Colorant	Color in PP	L	a	b	ΔE in PP
PBr 24	Yellow	57	7.0	40	2.6
PY 53	Yellow (whitish)	59	2.5	18	5.6
PO 78	Orange	54	10	18	0.9
PY 34	Yellow	58	−3.9	53	1.1
PY 180	Yellow	60	6.1	71	0.7
PR 177	Red	36	41	17	1.3
PB 60	Blue	27	11	−20	3.0

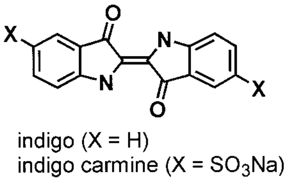

Figure 1 Chemical structures of natural indigo colorants.

with a rather dull shade and a moderate color strength at the applied concentration of 0.1 wt %. The benzimidazolone colorant PY180 is selected for being known as a high-temperature stable colorant with a pure hue.[25] PY180 mixed in PP yields a translucent sample with an excellent color brightness and color strength. The lead chromate based PY34 is tested as a colorant widely used in plastics until now.[27] It shows good color brightness and color strength. The amino-anthraquinone-based colorants PR177 and PB60 are evaluated as a reference because they have structural similarities with the natural anthraquinones alizarin and purpurin. Moreover, they are known for their application in automotive finishes because of their high weatherfastness and lightfastness, and they are said to exhibit excellent heat stability in plastics.[25] The PR177 yields a good color brightness and strength; the PB60 is somewhat dull in shade but has a good color strength. PY34, PR177, and PB60 all yield translucent PP samples. All these commercial reference colorants show homogeneous dispersion in PP.

From the high a- or b-values of, for example, amaranth, carmine, carmoisine, chlorophyllin, curcumin, erythrosine, henna, quinoline yellow, riboflavin, and sunset yellow (Table III), it can be concluded that several of the natural and synthetic food-approved colorants can, with respect to brightness, compete with a commercial colorant like PR177, which is applied in lead-free automotive finishes because of its full shade.[25] The aluminium lake of tartrazine can even compete with the benzimidazolone PY180, which is known for its very clean hue.[25]

Lightfastness in PP

The lightfastness is one of the most critical issues with regard to the long-term performance of colorants in plastics. The color change Δ*E* of the PP-samples after 48 h (UV) irradiation in a Suntest is taken as a measure for the lightfastness of the colorants. These values are presented in Table III. In Table IV, the lightfastness data of the tested inorganic and synthetic organic reference colorants are given.

The indigo and anthraquinone-based colorants proved to be the most light stable in the series of natural and synthetic food-approved colorants tested in PP. Chemical structures of these colorants are presented in Figures 1 and 2. The stability of indigo, alizarin, and purpurin can be explained from the possibility to form photostabilizing intramolecular hydrogen bonds.[23] Next in the line of decreasing light stability are the other natural colorants, completed by the synthetic food-approved colorants. With an exception for the aluminium lakes of quinoline yellow and indigo carmine, the synthetic food-approved colorants deteriorate easily in PP under influence of (UV) light. Saltmarsh refers to good light stability for the aluminium lakes of brilliant blue FCF, carmoisine, patent blue V, ponceau 4R, and sunset yellow in food environment, while the colorants fade nearly completely in PP after 48 h of Suntest irradiation.[19] On the other hand, Saltmarsh qualifies riboflavin and the aluminium lake of indigo carmine as light unstable in food applications, whereas this research shows good light stability for these colorants in PP. Regardless the processing temperatures—plastics are processed at temperatures as high as 200°C, whereas foods are generally processed below 100°C— it can be concluded that the "matrix" in which colorants are embedded very much determines the stability of the chemical structure of the colorants and, as a consequence, their ability to retain their color.

The change in color as a result of (UV) irradiation was also monitored by UV-VIS absorbance spectra. The UV-VIS absorbance spectra of the aluminium lakes of quinoline yellow and brilliant blue FCF in PP—both before and after 48 h Suntest irradiation—are presented in Figure 3. It can be concluded that 48 h of Suntest irradiation hardly changes the UV-VIS absorbance of quinoline yellow, whereas the absorbance of brilliant blue FCF is dramatically affected. The change in absorbance after irradiation is related to the breakdown of the chemical structure of the colorants. The UV-VIS absorbance data correspond well to the lightfastness, Δ*E*, of 5 and 38 for quinoline yellow and brilliant blue FCF, respectively.

The indigo and anthraquinone-based natural colorants have a light stability similar to the titanates and the indanthrone PB60. They do not, however, reach the lightfastness of the other inorganic and synthetic organic colorants tested (Table IV).

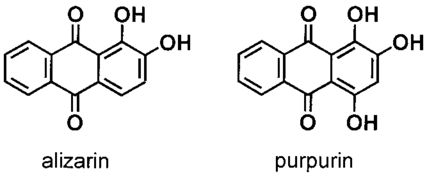

Figure 2 Chemical structures of natural anthraquinone colorants.

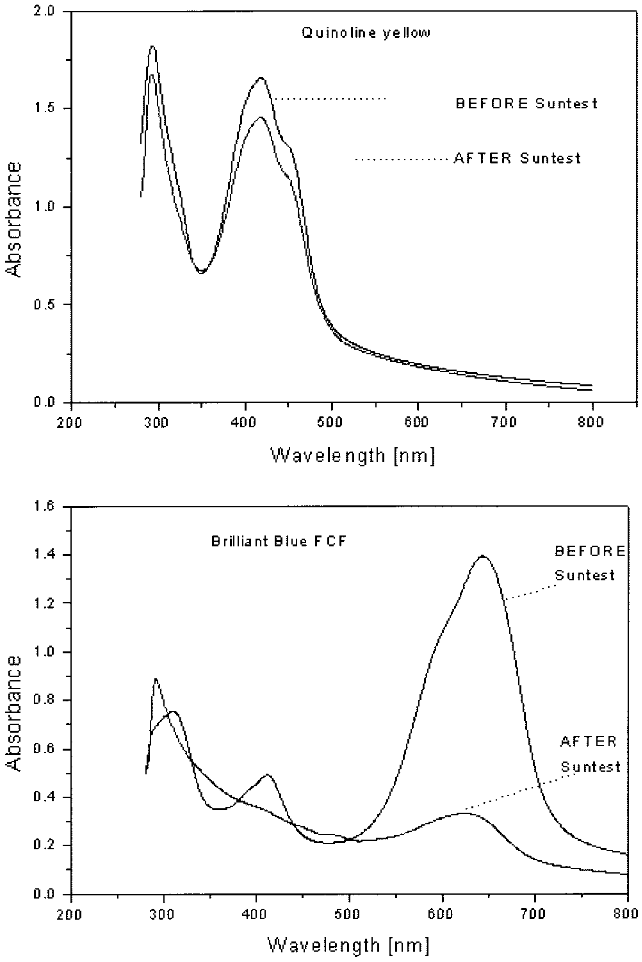

Figure 3 UV-Vis absorbance spectra of the aluminium lakes of quinoline yellow (A) and brilliant blue FCF (B) in PP before and after 48 h artificial (UV) irradiation in a Suntest.

Migration in PP

The translucent character of the colored PP samples indicates that the colorants are either dissolved in PP or are well-dispersed, very small particles with sizes below 50 nm.[26] In both cases, migration of colorants out of the polymer matrix may take place. To qualify the migration of colorants, colored PP samples have been put in a series of solvents: neutral, acidic (pH = 2.6) as well as alkaline (pH = 10) water, ethanol, sunflower oil, and hexane. After 10 days, the solvents have been analyzed using UV-VIS spectroscopy to determine bleeding of colorants into the solvent. After 60 days, the solvents have been analyzed again, and it has been concluded that after the first 10 days no significant amounts of colorant were further extracted from the PP. In ethanol, sunflower oil, and water—both neutral, acidic, and alkaline—no bleeding is observed. In hexane, however, alizarin, henna, and the chlorophyllin colorants show some bleeding from PP. Curcumin shows extensive bleeding.

When pressed against filter paper for 1 week, none of the colorants bled from the PP samples. On the other hand, the anthraquinones alizarin, and to a lesser extent purpurin, give a color to plastics in which the samples are stored for a couple of months. This is not observed for the other colorants, including those bleeding in hexane: henna, curcumin, and the chlorophyllin colorants.

Processing in PVC

Nearly all natural colorants and the aluminium lakes of the synthetic food-approved colorants disperse well in both the heavy metal-free PVC (HMF-PVC) and the lead-stabilized PVC (Pb-PVC) and yield opaque samples. An exception is indigo carmine in HMF-PVC, which gives small speckles in the sample. The sodium salts of the food grade colorants show poor dispersion as well. Migration of the colorants from PVC has not been observed.

In general, the color of the well-dispersed colorants in PVC is similar to the colored PP samples (Tables V and VI). However, the colored PVC samples have a lower brightness than the PP samples, which might be related to the opaque character of the PVC compounds. Exceptions are carmine, curcumin, purpurin, and riboflavin in the HMF-PVC and indigo in both PVC grades. This difference in color brightness can also be derived from the a- and b-color values of the PP and PVC samples. Lower color brightness corresponds to lower a- and b-color values. As in PP, the colorants based on plant tissues and of algal and fungal origin showed virtually no color in PVC.

Similar to the PP samples, alizarin, curcumin, and henna show a color change upon mixing in PVC. Alizarin turns purple in both PVC grades, probably as a result of deprotonation or metal complexation. For henna and curcumin, a color change to brown takes place during mixing in Pb-PVC, whereas in HMF-PVC, their color turns orange and remains yellow, respectively. This change in color is probably due to interaction with the lead component in the PVC compound.

The dynamic thermostability of HMF-PVC containing different natural colorants has shown to be similar to pure HMF-PVC during 20 min of kneading at 190°C.

Structural analog of natural colorants

Although the extensive screening of natural and food-approved synthetic colorants of this research has not resulted in a colorant with a performance equal to commercially applied colorants like PY34, PY180, PR177, and PB60, the best performing natural colorants come close. The best performing natural colorants are the natural anthraquinone and indigo-based colorants. They may form the basis for heavy metal and aromatic amine-free colorants. Therefore, the rel-

TABLE V
Color and L, a, b-Values, of Colorants, 0.1 wt % Mixed in Heavy Metal Free Stabilized PVC

Colorant	Color as pure colorant	Color in HMF-PVC	L	a	b
Alkannine	Blue	Purple (dark)	21	9.6	0.6
Alizarin	Yellow (brownish)	Purple	12	12	3.8
Brilliant Blue FCF, Al lake	Blue	Blue	35	−17	−5.7
Carmine	Red	Red (light)	38	34	16
Chlorophyllin	Green (greyish)	Green	39	3.6	22
Copper chlorophyllin YS	Green	Green	36	−7.8	17
Curcumin	Yellow	Yellow	69	−1.1	74
Erythrosine, Al lake	Pink	Pink	44	38	19
Henna	Yellow	Orange	51	31	51
Indigo	Blue	Blue	9.6	7.8	−16
Indigo carmine	Blue	Blue[a]	46	−11	14
Indigo carmine, Al lake	Blue	Blue	40	−16	−1.6
Ponceau 4R, Al lake	Red	Pink	46	29	23
Purpurin	Red (brownish)	Red	20	29	18
Quinoline Yellow, Al lake	Yellow	Yellow	63	3.5	50
Riboflavin	Yellow	Yellow	62	19	69
Sunset Yellow, Al lake	Orange	Orange	54	35	52
Tartrazine, Al lake	Yellow	Yellow	59	12	52
Chromium titanate	Yellow	Yellow[b]	72	8.5	48

[a] Limited dispersion.
[b] Pale shade.

atively cheap quinizarin (Fig. 4), a structural analog of alizarin and purpurin (Fig. 2), was evaluated as a colorant in PP and PVC. Moreover, quinizarin has an orange color, and may act as a basis for the much desired terra cotta color, which is currently based on lead chromate and molybdate orange.

Quinizarin has been processed into PP and HMF-PVC as described for the natural colorants. In PP, quinizarin turns into bright red and yields a translucent sample. The L,a,b-values of the colored PP sample are presented in Table VII. The light stability of quinizarin in PP is very similar to that of alizarin and purpurin, ΔE is 4.1 after 48 h of Suntest irradiation. This light stability is somewhat below the light stability of commercial amino anthraquinones PR177 and PB60 (Table IV).

In HMF-PVC, quinizarin yields a bright orange color, which can be applied as a basis for terra cotta

TABLE VI
Color and L, a, b-Values of Colorants, 0.1 wt % Mixed in Lead-Stabilized PVC

Colorant	Color as pure colorant	Color in Pb-PVC	L	A	b
Alizarin	Yellow (brownish)	Purple (dark)	18	10	−2.5
Amaranth, Al lake	Purple	Purple	44	21	−3.8
Brilliant Blue FCF, Al lake	Blue	Blue	48	−20	−16
Carmine	Red	Purple	44	21	−1.4
Carmoisine, Al lake	Red	Pink	47	28	4.3
Chlorophyllin	Green (greyish)	Green	35	1.3	20
Copper chlorophyllin YS	Green	Green	39	−14	16
Curcumin	Yellow	Brown (redish)	28	28	29
Erythrosine, Al lake	Pink	Pink	50	43	−2.2
Henna	Yellow	Brown (greyish)	41	9.7	12
Indigo	Blue	Blue	23	1.8	−22
Indigo carmine	Blue	Blue	50	−6.2	−14
Indigo carmine, Al lake	Blue	Blue	51	−8.0	−13
Patent Blue V, Al lake	Blue	Blue	47	−22	−16
Ponceau 4R, Al lake	Red	Pink	51	32	13
Quinoline Yellow, Al lake	Yellow	Yellow	72	−2.7	46
Riboflavin	Yellow	Yellow	66	11	44
Sunset Yellow, Al lake	Orange	Orange	59	28	32
Tartrazine, Al lake	Yellow	Yellow	67	8.5	44

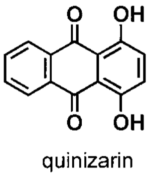

Figure 4 Chemical structure of quinizarin.

colors (Table VII) for which lead chromate/molybdate orange mixtures have been used during the past decades. To compare quinizarin with commercial lead chromate/molybdate orange, 0.1 wt % of these colorants has been extruded into HMF-PVC strips. To the quinizarin sample, organic red and carbon black have been added for tint reasons, 3 and 0.6 wt % with respect to quinizarin; 0.1 wt % TiO_2 has been added to the quinizarin sample to obtain opaque samples. The resulting strips had a brown-orange and orange color, respectively. The change in color of the quinizarin and lead chromate/molybdate PVC samples according to the Gray scale (conform ISO 105 A02) after 160–640 h aging in a Xenontester APP-403 (conform ISO 53387) is presented in Table VIII. These data indicate that quinizarin comes close to the lead chromate/molybdate orange performance.

Similarly colored lead chromate/molybdate and quinizarin HMF-PVC samples have been processed on a two-roll mill, followed by hot pressing to flat sheets. These colored PVC samples have been UV-irradiated in a QUV-tester. After 400 h of irradiation, the color change ΔE was 4 and 8 for quinizarin and lead chromate/molybdate, respectively (Table VIII). In this test quinizarin performs better than the commercial lead chromate/molybdate-based colorant. Combined with the low price for quinizarin of around \$5 per kg, quinizarin is an interesting alternative for lead chromate/molybdate orange colorants.

Also, in Pb and calcium/zinc (Ca/Zn)-stabilized PVC extrusion grades, quinizarin yields a bright orange color. The shade of the colors, however, is different from that of the HMF-PVC grade, as can be derived from the L,a,b-values (Table VII). In PVC injection-molding grades, which contain more alkaline components than extrusion-grade PVC, however, the color of quinizarin turned purple. This purple color is also observed when quinizarin is dissolved in an aqueous base solution. This indicates that deprotonation of quinizarin causes the color shift. Further research is under way to prevent color shift of quinizarin under alkaline conditions.

Like alizarin and purpurin, quinizarin shows bleeding in PP, although it does not in the different PVC grades tested. The degree of migration of colorants from the polymer matrix can be reduced by coupling the colorant to a nonmigrating substrate. In this study, quinizarin has been bonded onto reactive maleic anhydride-grafted PP (MAPP) by compounding 10 wt % of quinizarin in MAPP using the same process as has been used for mixing the colorants in PP. The MAPP is Epolene G-3015 of Eastman with an acid number of 15 mg KOH/g. The acid number is the amount of KOH required to neutralize one of the two carboxylic acid groups per MA unit for all MA units available per g MAPP. This means that the MAPP contains 2.6 wt % MA. If one quinizarin molecule chemically bonds to one carboxylic acid group of each MA unit, then 6.4 wt % of quinizarin can be bonded to the MAPP. Solvent extraction indicates that 7.5 wt % of the quinizarin has been bonded to the MAPP in such a way that it does not diffuse out of the MAPP after extensive extraction with ethanol. Mixing of 1 wt % of this colored MAPP in PP, which is equivalent to 0.1 wt % of quinizarin, results in a slightly diminished color intensity with respect to pure quinizarin. The color change ΔE with respect to the sample with pure quinizarin (see Table III) is 6, mainly as a result of increased L and b-color values. The bleeding, however, is nearly absent and the lightfastness remains unchanged, i.e., the ΔE after 48 h Suntest is 4. To entirely eliminate bleeding, it is necessary to optimize the bonding of quinizarin to MAPP or to extract unbonded colorant from the MAPP polymer before mixing in PP.

CONCLUSIONS

Over 20 natural and synthetic food approved colorants tested can endure processing in PP and PVC at temperatures as high as 180–200°C for 10 and 3 min, respectively, yielding bright colors with good color strength. Some colorants can endure processing in PP at 260°C.

The food-approved riboflavin and aluminium lakes of quinoline yellow and tartrazine have excellent color brightness in PP, which is close to the high-performing benzimidazolone PY180.

From the natural colorants evaluated in PP, the indigo and anthraquinone-based colorants are most light stable, i.e., similar to the titanates and the indanthrone PB60.

The colorants tested show no migration in neutral, acidic, and alkaline water, ethanol, and sunflower oil.

TABLE VII
L, a, b-Values and Color of 0.1 wt % Quinizarin, Mixed in PP, and Three PVC -Grades: Heavy Metal Free, Lead, and Calcium/Zinc-Stabilized PVC

Polymer	Color in polymer	L	a	b
PP	Red	33	46	44
HMF-PVC	Orange	51	37	67
Pb-PVC	Orange	59	34	67
Ca/Zn-PVC	Orange	49	38	64

TABLE VIII
Change in Color vs. Time According to Gray Scale after Xenontest and According to ΔE after QUV Test

Colorant	Color in HMF-PVC	Gray scale after Xenontest				ΔE after 400 h QUV test
		160 h	320 h	480 h	640 h	
Quinizarin	Orange (brownish)	3	3	3/2	2	4
Lead chromate/molybdate	Orange	5	4	3	3/2	8

The anthraquinones, curcumin, henna, and chlorophyllins show bleeding in hexane. The migration of colorants can be prevented by binding on a carrier material. Reduction of migration has been achieved for quinizarin bonded onto maleic anhydride-grafted PP.

Quinizarin, a structural analog of the natural anthraquinones alizarin and purpurin, yields a terra cotta color in PVC with a light stability that comes close to that of lead chromate/molybdate based colorants.

The best performing natural colorants meet the technical requirements for applications where moderate properties concerning heat resistance and (UV) light stability are required, such as indoor PP applications and PVC water drainage pipes.

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