Analytical Study of the Additives System in Polyethylene

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Synopsis

On the basis of standards the identification of substances in the additive system of polyethylene has been performed. Different methods for separation such as adsorption thin-layer chromatography, high-performance liquid chromatography with chemically bounded phases, and gas chromatography have been used. The final identification has been made with mass spectrometry. The substances have been extracted from polyethylene with hexane and chloroform.

INTRODUCTION

During their use, polyolefins are exposed to weathering that results in the gradual deterioration of their performance.[1] Degradation can be initiated by different impurities,[2] carbonyl,[3] or peroxide compounds.[4]

The production of polyolefins that do not contain these impurities is impossible, and, therefore, to hold the properties needed for their outdoor applications, it is necessary to incorporate into them additives inhibiting or retarding the destructive processes. Stabilization can be provided[5] by the addition of agents that absorb the harmful part of solar radiation and disperse the absorbed energy in the form of heat (UV absorbers), then by quenching the excited states of chromophors that initiate photodegradation or with quenching of singlet oxygen,[6] and by the inhibition of the radical processes (antioxidants) or by hydroperoxide decomposition. Practical applicability of a polymer depends on the amount and chemical structure of each component of the mixture of stabilizers.

Analytical procedures and problems related to the determination of additives in polymers have already been published in several articles.[7,8] Many analytical problems result from the following factors: from a more or less insoluble polymer matrix, from high reactivity and low stability of additives, and in many cases also from the low concentration of an additive in the polymer matrix. The first and the last factors need the separation of an additive from the polymer matrix.

Some authors have analyzed the additive system in a polymer by gel permeation[8] and liquid[9] chromatography. In our work the polyethylene additive system has been analyzed using high-performance liquid chromatography (HPLC) with chemically bounded phases. The results obtained by mass spectrometry and thermogravimetric analyses are also given.
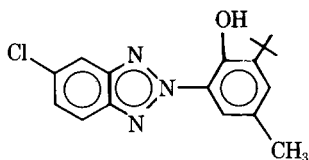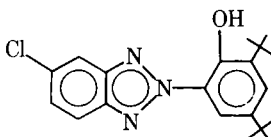
0021-8995/80/0025-1943$01.00

EXPERIMENTAL

In testing the individual analytical procedures the following standards have been used:
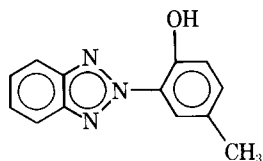
Tinuvin P

Tinuvin 326

Tinuvin 327
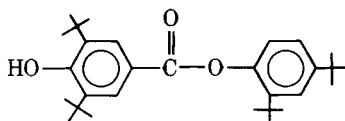
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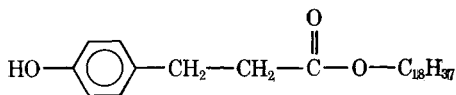
Irganox 1076
(Ciba-Geigy A.G.)
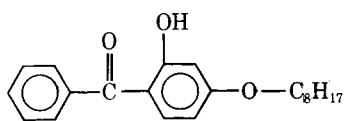
Cyasorb UV 531
(Amer. Cyanamid Co.)
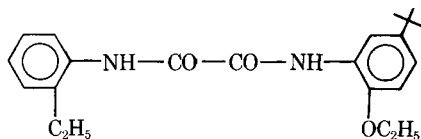
Sanduvor EPU
(Sandoz A.G.)
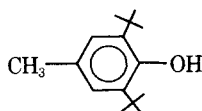
AO - 4 (Chemical Works of
G. Dimitrov, ČSSR)

Dastib 242 and Dastib 263 are the derivatives of 2-hydroxybenzophenone (development products of the Research Institute of Organic Technology, Bratislava, (ČSSR), and Anti UV-P is the 2-hydroxy-4-n-octyloxybenzophenone (Société Française d'Organo-Synthése).

Extraction has been chosen as a method for separation using a Soxhlet extraction apparatus. As to solvents, we have used n-hexane and chloroform dried by anhydrone and redistilled before the extraction was made. Powdered polyethylene (100 g) was extracted in 500 ml n-hexane for 12 hr. This was repeated three times, each time consisting of 12-hr extraction cycle being preceded by maceration for 12 hr. Every fraction was filtered and a filtrate was evaporated to dryness in a vacuum rotating evaporator (pressure 20 torr). The weights of individual evaporation residues were 2.061 and 0.306 g, respectively.

Then, on the base of lower solubility of low molecular PE in methanol, the soluble fractions of low molecular polymers were removed from the individual extracts. We pipetted 20 ml from an extract (total volume 100 ml) and added 100 ml methanol. The insoluble part was filtered in a porous glass filter where it was washed with an additional 50 ml of methanol. Then the filtrate evaporated to dryness was dissolved in 20 ml of chloroform.

As for separation techniques, we have studied the possibility of using different methods such as TLC, HPLC, and GC. Mass spectrometry has been taken as an identification method.

Thin-Layer Chromatography (TLC)

We have used commercially produced silica gel thin layers Silufol (Kavalier, Czechoslovakia). The adsorbent activation was performed for 1 hr at 120°C. The position of a substance after chromatography was investigated by different procedures. The most suitable was an agent containing ferric chloride which has caused blue or brown spots on the yellow base. (Directly before spraying the thin layer, 15% ferric chloride solution was blended with 1% potassium ferrocyanide solution in the ratio 1:1.) The substances that should not be detected in this way were sprayed on the thin layer with an agent composed of 7 g salicylic acid and 0.1 g ferric chloride dissolved in 25 ml water and 100 ml ethanol. After spraying, white spots have been detected on the black base (quoted).

High-Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography (HPLC) has been the other method applied to the separation of unknown substances in the extracts and for that of standard mixtures. We have used the Lichrosorb Si 60 10-μm column and the columns with chemically bounded phases designated as NH_2 and CN columns. Length and diameter of all of columns were 25 cm and 4 mm, respectively. The experiment has been performed with a Packard model 8200 device, and eluted substances have been detected by an UV detector at 254 nm. All solvents used were redistilled and dried by anhydrone.

Gas Chromatography (GC)

Another separation method chosen for the identification of substances in a polymer additive system was gas chromatography. We have used a Carlo Erba apparatus; a stationary phase was 2% SE-30 in Chromosorb WHP and the column length was 1.2 m. Detection has been made with a flame ionization detector.

Mass Spectrometry

Mass spectrometry has been used for the final identification of an unknown substance in a polymer additive system.

RESULTS AND DISCUSSION

The standards used had different physical and chemical properties, so that we had to investigate a greater number of mobile systems suitable always for a certain type of substance. The total evaluation of the results obtained by thin-layer chromatography has been used as an elimination step. If the measured values R_f of some standards were not approximately the same (± 0.1 of the value R_f) as the R_f of substances in the extract, the presence of these standards has been eliminated. In the systems 80% carbon tetrachloride–cyclohexane, the R_f values of all of Tinuvins are significantly different from the R_f values of unknown substances in the extract. The presence of other substances has been eliminated by similar procedure. The comparison of the R_f values of further substances such as Cyasorb 531, Dastib 263, Dastib 242, Anti UVP, and Irganox 1076 with the R_f values of unknown substances in the extract shows that they can be present in PE. It is evident that the last word about which of these substances is present in the extract will be said by other methods. The presence of Antioxidant-4 in the additive system has not been clearly proved. We must consider, however, that in the case of the possible trace concentration of this substance more sensitive methods should be used for its identification. Thin-layer chromatography has given approximate data about the presence of some substances in the polymer additive system. Some results obtained by thin-layer chromatography are given in Tables I and II.

The other method we have used to separate and identify the unknown substances in a polymer was high-performance liquid chromatography. To characterize the separated substance in the column we have calculated the value of the capacity ratio (k) according to

TABLE I

R_f Values of Some Standards and Extracts in Different Mobile Systems on Silica Gel Thin Layer Silufol

Sample	Mobile System					
	80% Carbon tetrachloride cyclohexane	Dioxane	Dichloro-methane	Isopropanol	Cyclohexa-none	50% dichloro-methane, cyclo-hexane
Tinuvin P	0.50	0.66	0.63	0.70	0.85	0.50
Tinuvin 120	0.86	0.66	0.72	0.70	0.85	0.71
Tinuvin 326	0.86	0.70	0.74	0.70	0.85	0.70
Tinuvin 327	0.86	0.65	0.73	0.70	0.85	0.71
Tinuvin 770	0.5	0.1	0.03			
Cyasorb UV 531	0.24	0.15	0.68		0.15	
Anti UV P		0.16	0.10			0.46
Hexane extract	0.27	0.15	0.69	0.59	0.19	0.48
	0.60[a]	0.52[a]	0.99[a]			0.92[a]
Chloroform extract	0.27	0.15	0.62	0.57	0.17	0.45

[a] Only in the trace concentration.

TABLE II
R_f Values of Some Standards and Extracts in Different Mobile Systems on Silica Gel Thin Layers Silufol

Sample	50% Cyclohexane dichloromethane	50% Carbon tetrachloride, dichloromethane	30% Chloroform cyclohexane	50% Chloroform cyclohexane	70% Chloroform cyclohexane	3% Propanol, hexane
Irganox 1076			0.20	0.70	0.83	
Cyasorb UV 531			0.15	0.51	0.59	
Anti UV P	0.46	0.86		0.48		0.40
Sanduvor EPU	0.1	0.15		0.1–94		0.73
		0.65				
AO-4	0.97	0.92		1.00		
Dastib 242			0.15	0.50	0.63	
Dastib 263			0.15	0.50	0.62	
Hexane extract	0.46	0.85	0.14	0.56	0.58	0.42
	0.96[a]	0.90[a]	0.58[a]	0.98[a]	1.00[a]	0.90[a]
Chloroform extract	0.45	0.84		0.54		0.42

[a] Only in the trace concentration.

$$k = (V_x - V_0)/V_0$$

V_x is the elution volume of the given substance and V_0 is the dead volume of the column calculated from the elution volume value of a substance that has not been retained in the column (e.g., hexane, benzene, chloroform). To obtain as much information as possible for the final identification of unknown substances, the value of capacity ratios were measured in each type of the column in different mobile phases. Tables III–V give some capacity ratio values of the standards used which have been compared with the value of capacity ratios of unknown substances in the extracts. On the basis of these results we can draw preliminary conclusions as to which substances are present in the sample. We took into

TABLE III
Values of Capacity Ratios of Some Standards and Extracts in Different Mobile Systems;
Column: Lichrosorb Si 60

Sample	10% $CHCl_3$-cyclohexane	30% $CHCl_3$-cyclohexane	Chloroform
Tinuvin P	0.26	0.24	0.05
Tinuvin 120	0.10	0.00	0.00
Tinuvin 326	0.10	0.00	0.00
Tinuvin 327	0.12	0.00	0.00
Cyasorb UV 531	0.58	0.22	0.04
Anti UV P	0.57	0.22	0.04
Sanduvor EPU	0.11; 0.25	0.51; 0.39	0.00
AO-4	0.11	0.09	0.00
Dastib 242	0.34	0.13	0.03
Dastib 263	0.57	0.21	0.03
Hexane extract	0.50	0.22	0.03
	0.09[a]	0.06[a]	
Chloroform extract	0.58	0.18	0.03

[a] Only in the trace concentration.

TABLE IV
Values of Capacity Ratios of Some Standards and Extracts in Different Mobile Systems;
Column: NH_2

Sample \ Mobile system	Cyclohexane	5% dichloromethane-cyclohexane	2% chloroform-cyclohexane	2% chloroform-heptane
AO-4	0.42	0.07	0.21	0.24
Tinuvin 326	2.80	0.70	1.20	1.31
Tinuvin 327	2.80	0.68	1.30	1.35
Cyasorb UV 531	7.45	0.90	4.27	4.37
Anti UV P	7.40	0.92	3.31	3.83
Dastib 242	7.21	0.81	4.20	4.22
Dastib 263	7.22	0.81	4.15	4.27
Hexane extract	0.40[a]	0.03[a]	0.18[a]	0.22[a]
	7.35	0.93	4.30	4.34
Chloroform extract	7.40	0.90	4.33	4.40

[a] Only in the trace concentration.

consideration the following substances: Cyasorb UV 531, Dastib 263, Dastib 242, and AO-4 in the trace concentrations. Comparing the results obtained by thin-layer chromatography with those of high-performance liquid chromatography indicates that they are in a good agreement and that a number of substances pointed out by the first procedure have been reduced. Detection limits were about 7 mg in 100 ml chloroform.

Gas chromatography has been taken as a further method for the identification of substances in the extract. The results obtained by thermal analyses showed the possibility of using this procedure. It has been proven that the evaluated substances are thermally resistant to heat even at temperatures of about 300°C in the inert atmosphere. Table VI presents the values of capacity ratios of some standards and substances in the extracts.. The comparison of the values of capacity ratios of standards with those of capacity ratios of substances in the extract correspond to higher hydrocarbons originating from the low-molecular-weight

TABLE V
Values of Capacity Ratios of Some Standards and Extracts in Different Mobile Systems;
Column: CN

Sample \ Mobile system	Cyclohexane	5% $CHCl_3$-cyclohexane	10% $CHCl_3$-cyclohexane
Tinuvin P	0.62	0.41	0.00
Tinuvin 120	2.71	1.01	0.00
Tinuvin 326	0.01	0.00	0.00
Tinuvin 327	0.01	0.00	0.00
Cyasorb UV 531	1.95	0.95	1.30
Anti UV P	1.95	0.91	1.24
AO-4	0.53	0.20	0.00
Dastib 242	1.91	1.00	0.63; 0.96
Hexane extract	0.50[a]	0.21[a]	0.00[a]
	1.96	1.01	1.37
Chloroform extract	1.90	0.98	1.01

[a] Only in the trace concentration.

TABLE VI
Values of Capacity Ratios (Gas Chromatography) of Some Standards
(Column SE − 30; $T = 290°C$)

Sample	Capacity ratio
Tinuvin 770	20.38
Tinuvin 327	8.01
Tinuvin 326	6.75
Dastib 242	8.50
Cyasorb UV 531	11.71
AO − 4	5.10[a]
Chloroform extract	13.70; 11.80; 7.66; 3.34; 2.50;

[a] Measured at 180°C.

fraction of polyethylene. The value of capacity ratio of another substance which could not be separated by another method (Dastib 242) are significantly different from the value of the Cyasorb 531 capacity ratio which even more clearly proves its presence in the sample. Gas chromatography analysis of additional substances was not successful at the given conditions but it was not necessary for the identification of substances in the extract, since their presence in a polymer has been eliminated by the preceding methods.

Mass spectrometry has been used for the final identification of Cyasorb 531 in the extracts from polyethylene. To retain all substances in the extract and especially to identify molecular ions, experiments were made gradually at 60, 65, and 70°C at a low ionization energy of 10 eV. At 60°C in the mass spectrum, peaks were studied at $m/e = 224$ and 326. These maxima correspond to $C_{16}H_{32}$ and Cyasorb 531. Lines were also generated at $m/e = 269, 310, 324, 338, 352,$ and 366, and these correspond to alcanes from $C_{21}H_{44}$ to $C_{26}H_{54}$. A similar spectrum to the preceding one has been obtained at 70°C also, but the difference was in generating two further maxima $m/e = 380$ and 394 corresponding to alcanes $C_{27}H_{56}$ and $C_{28}H_{58}$ originating from the low-molecular-weight parts of polyethylene. The ionization potential was then increased to 14 eV because the investigation also gives individual fragments of molecules, the presence of which were supposed on the basis of the preceding spectra. Based on a spectrum of the standard, the presence of Cyasorb 531 has been very reliably proven according to fragments at $m/e = 214, 213, 137, 105,$ and 77. The presence of the mentioned hydrocarbons has been clearly proven; as to the question of the presence of Antioxidant-4, we have not been successful in solving it by mass spectrometry. One of the possible reasons can be the very low concentration of this substance, which is consistent with the results obtained by preceding methods, and its very high evaporation rate, which can be predicted from the thermal analysis results.

CONCLUSIONS

In our experiments we have used methods suitable for the qualitative as well as quantitative analysis of additives in the polymer on the basis of their comparison with known standards. High-performance-liquid chromatography and gas chromatography, together with mass spectrometry, make possible the qualitative and quantitative analyses of additives for studying the quality of the produced polymer, as well as the changes which are generated in antioxidants

and stabilizers during processing and weathering. Though GC and HPLC can be used for rapid analysis, the total period within the course of which the analysis is performed depends on the time necessary for extraction of additives from the polymer.

References

1. H. J. Heller, *Eur. Polym. J. Suppl.*, 105 (1969).
2. O. Cicchetti, *Adv. Polym. Sci.*, **7**, 70 (1970).
3. D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 587 (1969).
4. D. J. Carlsson, D. M. Wiles, *Macromolecules*, **2**, 597 (1969).
5. A. M. Trozzolo, in *Polymer Stabilization*, W. L. Hawkins, Ed., Interscience, New York, 1972, chap. 4.
6. P. Hrdlovič, J. Daněček, M. Karvaš, and J. Durmis, *Chem. Zvasti*, **28**, 792 (1974).
7. T. R. Crompton, *Chemical Analysis of Additives in Plastics*, Pergamon, Oxford, 1971.
8. M. M. Wims, S. J. Swarin, *J. Appl. Polym. Sci.*, **19**, 1243 (1975).
9. J. M. Howard III, *J. Chromatogr.*, **55**, 15 (1971).