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# POLYPROPYLENE PIPES FOR DRINKING WATER SUPPLY

Ch. Hametner[a]
[a] Austrian Plastics Institute, Vienna, Austria

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# POLYPROPYLENE PIPES FOR DRINKING WATER SUPPLY

**Ch. Hametner**

Austrian Plastics Institute
Franz-Grillstr. 5
A-1030 Vienna, Austria

## ABSTRACT

Within this study, the influence of the migration of phenolic antioxidants, which are typically used for the stabilization of PP pipes, on the quality of drinking water has been tested. In particular, it had to be shown if the high requirements for materials in contact with drinking water can also be assured in the case of warm water and more alkaline or acidic drinking water.

The used migration procedures are based on Austrian, German, and international standard methods for cold water at 23°C and for warm water at 60°C. In addition to the migration of phenolic substances, the content of total organic carbon (TOC) and the threshold odor (TON) and flavor number (TFN) have been determined.

In general, not the high molecular antioxidants, but the low molecular degradation product 2,4-di-t-butylphenol was detectable in the aqueous extracts. In warm water extracts, the concentration of phenols, TOC, and also the influence on odor and flavor were considerably higher than in a cold one. Alkaline water extracted higher amounts of phenols, whereas acidic drinking water showed no effect.

Thermal load of the material during the extruding procedure leads to a significant increase of extractable phenols, TOC, and TFN/TON.

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## INTRODUCTION

The high heat distortion temperature and the high durability at long time high temperature load makes polypropylene an interesting material for use for the drinking water supply, especially under warm water conditions.

Within this study, the influence of the migration of phenolic antioxidants normally used for the stabilization of PP-pipes and possible phenolic degradation products of these antioxidants on the quality of drinking water were to be determined. For the migration procedure methods have been applied, which are required for drinking water certification in Austria and Germany. But also new European and International standards, which are presently in draft status, have been used. The content of extractable phenolic substances, the total organic carbon (TOC) and also the threshold odor (TON) and flavor number (TFN) of the test water were chosen as characteristic values for material properties in contact with water. The extractable phenolic substances should also be identified.

Additionally, the influence of temperature and the pH of the drinking water on the test parameters should be determined.

## EXPERIMENTAL

### Instruments

Gas chromatograph Hewlett Packard HP 5890, coupled with mass selective quadrupol detector HP 5971A or flame ionization detector, phenyl methyl silicon column

Spectral photometer HACH DR 3000
TOC-Analyzer Dohrmann DC-180
Oven, 60 ± 2°C

### Materials

For testing purposes, the following pipe samples with an inner diameter of 40 mm were used:

- Five different types of commercially available PP pipes produced at a mass temperature of 220°C (No. 1, 2, 3, 4, and 7)
- One pipe similar to No. 1, but additionally grey colored in a second thermal step at 220°C (No. 5)
- One new, not even commercially available type, produced at a mass temperature of 220°C (No. 6)

- One pipe similar to No. 2, but extruded at a mass temperature of 240°C (No. 8)

## Methods

### *Migration tests according to ÖNORM B 5014/1 [1], KTW recommendations [2] and ISO/FDIS 8795 [3] at 23 ± 2°C*

The test pieces were pretreated by filling with tap water, stored for a period of 24 hours at room temperature, and washed for two hours in a flow of tap water. For the actual migration test, the pipes were filled with test liquid for a migration period of 72 hours at 23°C three times. The test water was then decanted and subjected to the analysis of constituents as described below (see sections on "Migration Tests According to prEN 1420, etc." to "Analysis of Leachable Phenolic, etc.").

As a test liquid, water conforming to grade 3 of ISO 3696:1987 was used. For testing the influence of pH on the migration of phenols, the following test liquids were used:

– acidic water adjusted to a pH of 4,5 with $KH_2PO_4$ buffer solution
– alkaline water adjusted to a pH of 9,0 with boric acid buffer solution

### *Migration tests according to ISO/FDIS 8795 at 60 ± 2°C*

The test pieces were pretreated by filling with tap water, stored for a period of 7.5 hours, and then for 16 hours with fresh water, both at a temperature of 60 ± 2°C, and washed for two hours in a flow of tap water. For the actual migration test, the pipes were filled with test liquid for a migration period of 72 hours at 60 ± 2°C three times. The test water was then decanted and subjected to the analysis of constituents as described below (see sections on "Migration Tests According to prEN 1420, etc." to "Analysis of Leachable Phenolic, etc.").

As a test liquid, water conforming to grade 3 of ISO 3696:1987 was used.

### *Migration tests according to prEN 1420/1 [4] at 60 ± 2°C for estimation of TFN and TON*

The preliminary treatment consisted of filling the test pieces with tap water, storing for a period of 24 hours at 23°C, washing for 60 minutes in a flow of tap water, then storing for 7.5 hours and finally with fresh water for 16 hours, both at a temperature of 60 ± 2°C. For the actual migration test, the pipes were filled with test liquid for a migration period of 24 hours at 60 ± 2°C three times.

TABLE 1. Characteristics of the HPLC Method for Determination of Leachable Antioxidants

| Column | Hypersil 130 S-C18 | | |
|---|---|---|---|
| Oven temperature | 27°C | | |
| Injection volume | 20 µl | | |
| Eluent | gradient | | |
| | water<br>20/5 | etylacetate<br>10/90 | methanol<br>70/5 |
| Flow | 1.5 ml/min | | |
| Detection | UV 270 nm | | |

After this contact, the migration water was assessed by a test panel to determine the TON and TFN according to ÖNORM EN 1622 [5].

### *Analysis of leachable antioxidants (HPLC method)*

200 ml of test water was extracted with 5 ml of n-hexane for 30 minutes. The dried solvent extract was reduced to an amount of 0.5 ml and analyzed by HPLC using UV detection. The characteristics of the method are given in Table 1.

### *Analysis of leachable low molecular degradation products (GC method)*

*200 ml* of test water was extracted with 5 ml of n-hexane for 30 minutes. The dried solvent extract was reduced to an amount of 0.5 ml and analyzed by GC using FID or mass selective detection. The characteristics of the method are given in Tables 2 and 3.

### *Analysis of leachable phenolic substances according to standard method DIN 38409/16 [6]*

500 ml of test water were adjusted to a pH of 10 by use of 20 ml of buffer solution, and 3 ml of aminoantipyrine solution and 3 ml of peroxodisulfate were added. After 30 minutes, the colored reaction product was extracted with 25 ml of chloroform. The extinction of the solvent extract was measured at 460 nm by use of a spectrophotometer. In contrast to the DIN method, the calibration was carried out with standard solutions of 2,4-di-tert.butylphenol instead of phenol. The analysis characteristics are summarized in Table 4.

TABLE 2. Characteristics of the GC Method for Analysis of 2,4-di-tert.butylphenol

| **Column** | Phenyl Methyl Silicon |
|---|---|
| **Temp. program** | 100-200°C |
| **Column Head Pressure** | 100 kPa |
| **Injector temp.** | 300°C |
| **Detector temp.** | 300°C |
| **Detector** | FID |

### *Determination of TOC according to ÖNORM EN 1484 [7]*

The TOC determination was carried out by use of a TOC Analyzer based on the chemical oxidation of organic substances using 2% peroxodisulfate solution in the presence of UV radiation. The carbon dioxide formed is detected by a NDIR spectrometer. Calibration was carried out using potassium hydrogenphthalate standard solutions.

## RESULTS AND DISCUSSION

High molecular antioxidants could be detected only in traces in a range of about 1-2 ppb in the test water of two pipe samples (Nos. 3 and 7). In most

TABLE 3. Analysis Characteristics for 2,4-di-tert.butylphenol with GC Method

|  | Detection Limit | Determination Limit | Standard Deviation |
|---|---|---|---|
| 2,4-di-tert.butylphenol | 0.8 µg/l | 3 µg/l | 0.5 |
| recovery | 91% |  |  |

TABLE 4. Analysis Characteristics for Assessment of 2,4-di-tert.butylphe-nol With Spectralphotometric Method

| | **Detection Limit** | **Determination Limit** | **Standard Deviation** |
|---|---|---|---|
| 2,4-di tert.butylphenol | 3 µg/l | 5 µg/l | 1.3 |

warm water extracts, the degradation product 2,4-di-t-butylphenol could be detected, which can be built by the hydrolysis of antioxidants based on phosphites and phosphonites. The highest concentration could be detected in the extracts from pipes no. 5 and 8. Both of them differ from the other samples in their processing conditions: pipe no. 5 needed a second thermal step for coloring, pipe 8 was extruded at a higher mass temperature (240°C). Also, the TOC values of the warm water extracts and the influence on flavor and odor were significantly higher (Tables 6 and 7).

Under cold water conditions, all pipe samples meet the limits according to ÖNORM B 5014/1 in the third migration period, which is decisive for the assessment. If these limits were also valid for warm water tests according to ISO/FDIS 8795, only five of eight pipes could fulfill the requirements for TOC of 0.75 mg/l. The limit of ÖNORM B 5014/1 of 75 µg phenoles per litre were met by all pipe samples. The very low limit of the European drinking water regulation RL 80/778 for phenols in drinking water of 0.5 µg phenols per litre is below

TABLE 5. Results of the Testing of Pipe No. 5 at Two Different Ph Conditions

| pH | 1st Migration | 2nd Migration | 3rd Migration |
|---|---|---|---|
| | 2.4 | 2.4 | 2.4 |
| 9 | 13 µg/l | 14 µg/l | 7 µg/l |
| 4,5 | 2 µg/l | <1 µg/l | <1 µg/l |

PI.......phenol index
2.4.....2.4-di-t-butylphenol

TABLE 6. Results According to ÖNORM B 5014/1 at 23 ± 2°C

| Pipe No. | 1st Migration | | | | | 2nd Migration | | | | | 3rd Migration | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TOC | PI | 2.4 | TON | TFN | TOC | PI | 2.4 | TON | TFN | TOC | PI | 2.4 | TON | TFN |
| | mg/l | µg/l | µg/l | --- | --- | mg/l | µg/l | µg/l | --- | --- | mg/l | µg/l | µg/l | --- | --- |
| 1 | <0.1 | <3 | 5 | 4 | 3 | <0.1 | <3 | 4 | 4 | 2 | <0.1 | <3 | 4 | 4 | 2 |
| 2 | <0.1 | <3 | 1 | 2 | 2 | 0.3 | <3 | <1 | 2 | 1 | <0.1 | <3 | <1 | 1 | 1 |
| 3 | <0.1 | <3 | 3 | 2 | 2 | | <3 | 2 | | | | <3 | <1 | | |
| 8 | <0.1 | <3 | 2 | 2 | 2 | 0.2 | <3 | 1 | 2 | 1 | <0.1 | <3 | <1 | 2 | 1 |
| 5 | <0.1 | <3 | 1.5 | 3 | 2 | <0.1 | <3 | <1 | 4 | 1 | <0.1 | <3 | | 3 | 1 |
| 6 | <0.1 | <3 | 2 | 2 | 2 | | <3 | 4 | | | | <3 | <1 | | |
| 7 | <0.1 | <3 | 2 | 2 | 2 | 0.3 | <3 | 3 | 3 | 1 | <0.1 | <3 | 2 | 2 | 1 |
| 8 | 0.1 | <3 | 5 | 3 | 2 | 0.4 | 7 | 3 | 4 | 2 | 0.1 | <3 | <1 | 3 | 1 |

the detection limit of both applied methods (DIN 38409/16 and the GC method developed by us, cf. section "Analysis of Leachable Antioxidants, etc."). But, nevertheless, in most cases, phenol could be identified in the third migration test.

In contrast to neutral media, alkaline water extracted higher concentrations of 2,4-di-tert.butylphenol, whereas acidic drinking water showed no effect (Table 5).

TABLE 7. Results According to ISO/FDIS 8795(TOC, PI, 2,4) and prEN 1420/1 (TON/TFN) at 60 ± 2°C

| Pipe No. | 1st Migration | | | | | 2nd Migration | | | | | 3rd Migration | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | TOC | PI | 2.4 | TON | TFN | TOC | PI | 2.4 | TON | TFN | TOC | PI | 2.4 | TON | TFN |
| | mg/l | µg/l | µg/l | --- | --- | mg/l | µg/l | µg/l | --- | --- | mg/l | µg/l | µg/l | --- | --- |
| 1 | 1.0 | 13 | 4 | 5 | 3 | 0.3 | <3 | 5 | 4 | 3 | 0.3 | <3 | <1 | 3 | 2 |
| 2 | 0.4 | 6 | 1 | 4 | 2 | 0.3 | <3 | <1 | 3 | 3 | 0.2 | <3 | <1 | 3 | 2 |
| 3 | 0.7 | 3 | <1 | 4 | 3 | 0.3 | <3 | 2 | 4 | 3 | 0.2 | <3 | 1 | 3 | 2 |
| 4 | 0.6 | 13 | 7 | 3 | 3 | 1.4 | <3 | 4 | 3 | 4 | 1.0 | <3 | 2 | 3 | 2 |
| 5 | 3.3 | 21 | 15 | 4 | 3 | 1.4 | 3 | <1 | 6 | 5 | 0.8 | <3 | 5 | 5 | 3 |
| 6 | 0.3 | <3 | 1 | 4 | 3 | 0.1 | <3 | 4 | 4 | 3 | 0.1 | <3 | <1 | 3 | 2 |
| 7 | 0.5 | <3 | 2 | 2 | 3 | 0.3 | <3 | 5 | 4 | 3 | 0.2 | <3 | 3 | 3 | 2 |
| 8 | 10.5 | 19 | 5 | 5 | 4 | 1.4 | 16.5 | 15 | 4 | 4 | 1.1 | 5 | 3 | 4 | 3 |

## CONCLUSION

In summary, not the high molecular antioxidants, but the low molecular degradation product 2,4-di-t-butylphenol was detectable in the aqueous extracts. In warm water extracts, the concentration of phenols, TOC and also the influence on odor and flavor were much higher than in cold. Alkaline water extracted higher amounts of phenols, whereas acidic drinking water showed no effect.

Thermal load of the material during the extruding procedure leads to significant increase of extractable phenols, TOC and TFN/TON.

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[4] FINAL DRAFT prEN 1420-1: Influence of organic materials on water intended for human consumption - Determination of odor and flavor assessment of water in piping systems - Part 1: Test method (July, 1997).

[5] ÖNORM EN 1622: Water analysis - Determination of the threshold odor number (TON) and threshold flavor number (TFN).

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