Designation: D4676 – 94 (Reapproved 2012)

Standard Classification for Rubber Compounding Materials—Antidegradants[1]

This standard is issued under the fixed designation D4676; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This classification covers antidegradants used in rubber and where appropriate defines their important chemical and physical characteristics for use in rubber.

1.2 The general term "antidegradant" describes materials used in rubber to protect against the effects of oxygen and ozone. Materials that fall in this general category include both antioxidants and antiozonants.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1218 Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids

D1519 Test Methods for Rubber Chemicals—Determination of Melting Range

D1747 Test Method for Refractive Index of Viscous Materials

D2702 Practice for Rubber Chemicals—Determination of Infrared Absorption Characteristics

D3461 Test Method for Softening Point of Asphalt and Pitch (Mettler Cup-and-Ball Method)

D4571 Test Methods for Rubber Compounding Materials—Determination of Volatile Material

D4574 Test Methods for Rubber Compounding Materials—Determination of Ash Content

D4937 Test Method for*p*-Phenylenediamine Antidegradants Purity by Gas Chromatography

D5376 Test Method for Rubber Compounding Materials—Determination of the Basic Nitrogen Content in Rubber Antioxidant: Polymerized TMQ

E28 Test Methods for Softening Point of Resins Derived from Pine Chemicals and Hydrocarbons, by Ring-and-Ball Apparatus

3. Significance and Use

3.1 There are many different antidegradants available for use in the rubber industry.

3.2 This classification of the various materials covers their chemical structure along with a brief reference to their overall use and their properties.

4. Basis of Classification

4.1 Rubber antidegradants included in this classification document are divided into the six classes shown below. The classification in general is based on the chemical structure categorization but in most cases it also classifies the materials according to their potential rubber applications.

4.2 *Class 1, p-Phenylenediamines (PPDs)*—This group of additives represents the primary materials used in tires and other mechanical goods to impart ozone protection. These additives are also used as antioxidants and antiflex agents in a number of applications but are considered to be strongly staining and thus limited to black rubber applications. They can also be used as raw polymer stabilizers.

4.2.1 Although all PPDs have similar performance characteristics, the different types are frequently preferred for certain end use conditions; for example, selection is based on the type and degree of flexing to be experienced by the rubber article.

4.3 *Class 2, Trimethyl-dihydroquinolines (TMQs)*—These materials are primarily used to protect rubber articles from degradation by atmospheric oxygen at higher temperatures. They are moderately staining.

4.3.1 Although all TMQs have similar performance characteristics, different types are frequently preferred to accommodate processing or end use needs.

4.4 *Class 3, Phenolics*—Phenolic antidegradants represent a group of "nonstaining" and "nondiscoloring" additives used primarily in light colored mechanical goods and tires. They can also be employed as raw polymer stabilizers. The term "nondiscoloring" is used somewhat loosely, as products yielding

[1] This classification is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.20 on Compounding Materials and Procedures.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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slight discoloration are included in this classification. This is done to distinguish them from the strongly staining and discoloring amine type antidegradants (for example, PPDs).

4.4.1 The different types of phenolic antidegradant afford varying degrees of protection against oxidation, heat aging, rubber "poisons," and crazing. In general they are weaker antioxidants than the staining amines types.

4.5 *Class 4, Alkylated Diphenylamines (DPAs)*—This class of additives is generally considered representative of substituted amine antioxidants and they are used as raw polymer stabilizers and in vulcanizate applications. They are moderately discoloring and staining.

4.6 *Class 5, Aromatic Phosphites*—These are phosphorous containing fully nonstaining-nondiscoloring additives used as stabilizers for synthetic elastomers in "white rubber" applications. They also have application as peroxide decomposers and radical traps in many polymer systems.

4.7 *Class 6, Diphenylamine-Ketone Condensates*—This group of additives is used primarily in carbon black loaded compounds to protect against both oxygen and heat deterioration.

5. Basic Description of Antidegradants

5.1 *p-Phenylenediamines*—The individual materials in the class of compounds designated as *p*-phenylenediamines vary in chemical structure and in performance characteristics depending on the substitution on the nitrogen atoms in the parent compound, *p*-phenylenediamine. The three general types of PPDs used in rubber are defined below:

5.1.1 *PPD Type I: N,N'-dialkyl-p-phenylenediamines (see* Fig. 1*)*—*R* and R_1 are secondary alkyl groups, usually *C*6 or larger. These additives are generally liquids at ambient conditions and represent single chemical components (>90 %).

5.1.2 *PPD Type II: N-alkyl-N'-aryl-p-phenylenediamines (see* Fig. 2*)*—*R* is a secondary alkyl group and R_1 is hydrogen or a primary alkyl substituent (usually methyl). These products generally consist of a single component or purposeful mixture of two or more major components. They can be either liquids or solids.

5.1.3 *PPD Type III: N,N'-diaryl-p-phenylenediamines (see* Fig. 3*)*—*R* and R_1 can be the same or different groups consisting of hydrogen or alkyl groups (usually methyl). Therefore, this type can be individual components or mixtures of three or more isomers. This type of PPD is generally solid at ambient conditions.

5.2 *Trimethyl-dihydroquinolines*—Compounds designated as TMQs represent a group of antidegradants based on polymerized aniline-acetone condensation products. The individual products differ by the degree of polymerization as well as the ratio of aniline to acetone in the monomer preparation.

5.2.1 Since these products are complex mixtures they are best described with chemical reactions (see Fig. 4).

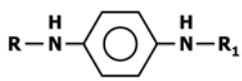

FIG. 1 Type I—N-N'-dialkyl-*p*-phenylenediamines

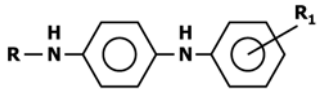

FIG. 2 Type II—N–alkyl–N'–aryl–*p*–phenylenediamines

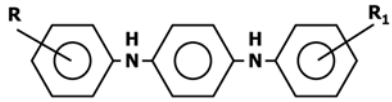

FIG. 3 Type III—N,N'–diaryl– *p*–phenylenediamines

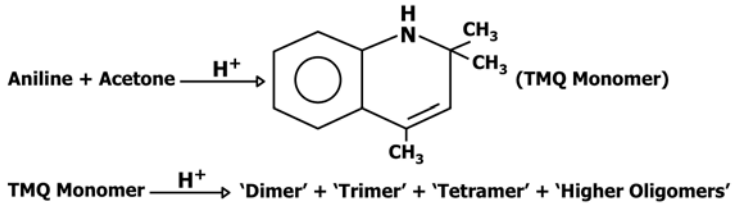

FIG. 4 TMQ Chemistry

5.2.2 The generally accepted chemical structure for TMQ oligomers (polymers) is given in Fig. 5.

5.2.3 Alternate structures may also be present containing aniline end groups or acetone bridges, or both, as shown in Fig. 6.

5.2.4 Other complex structures are also present in all TMQ products. The precise nature of the oligomeric mixture is a function of the monomer preparation conditions, monomer purification, and polymerization conditions.

5.3 *Phenolics*—Phenolic antioxidants are classified chemically according to the number of phenolic groups in the molecule. In general the more sterically hindered phenolic antioxidants are less discoloring but have lower antioxidant activity in rubber applications.

5.3.1 *Monofunctional phenols (Type I)* are frequently referred to as hindered phenols. They develop little discoloration however they show the weakest antioxidant activity and are relatively volatile due to the low molecular mass. Their primary use is as polymer stabilizers. In the general structure (see Fig. 7), R_1, R_2, and R_3 can be hydrogen, alkyl, aryl, aralkyl, or thioalkyl groups, or a combination thereof. These groups may also contain carboxylic acid esters, thioesters, or triazine functions.

5.3.2 *Bifunctional phenols (Type II)* are also referred to as hindered bisphenols. They represent the most important class of phenolic antioxidants used in rubber applications. In general they have good antioxidant activity with minimal discoloration. In the general structure (see Fig. 8 and Fig. 9), the *R* groups are normally located in the "ortho" or "para" position in relation to the phenol function. *R* is generally alkylidene

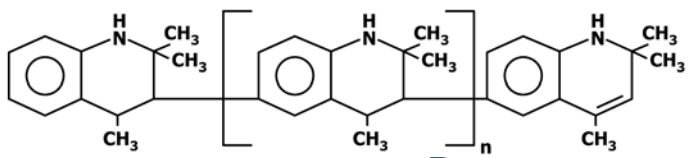

FIG. 5 TMQ Oligomeric Structure

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