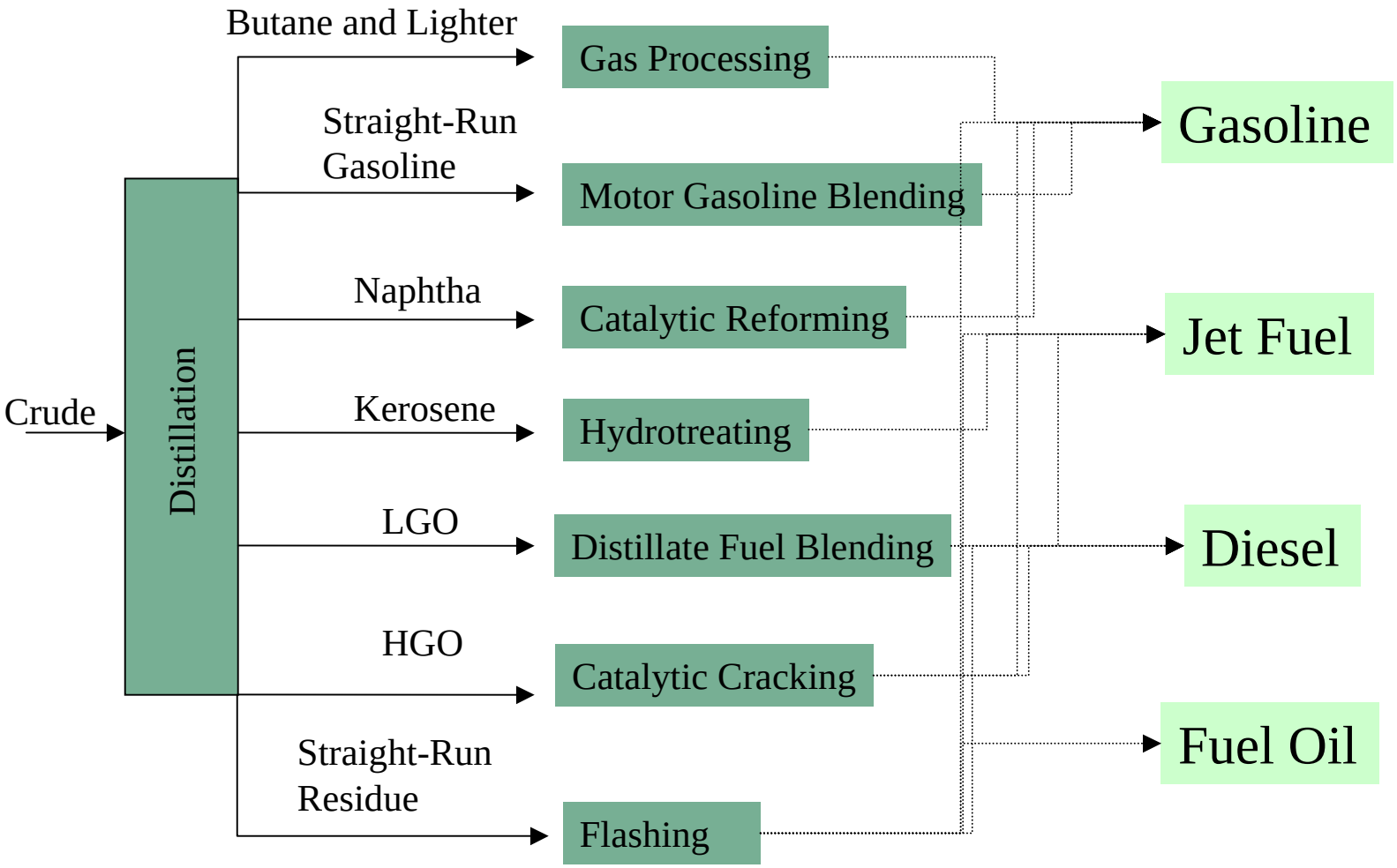
ETHANOX Fuel Antioxidants

October 2005

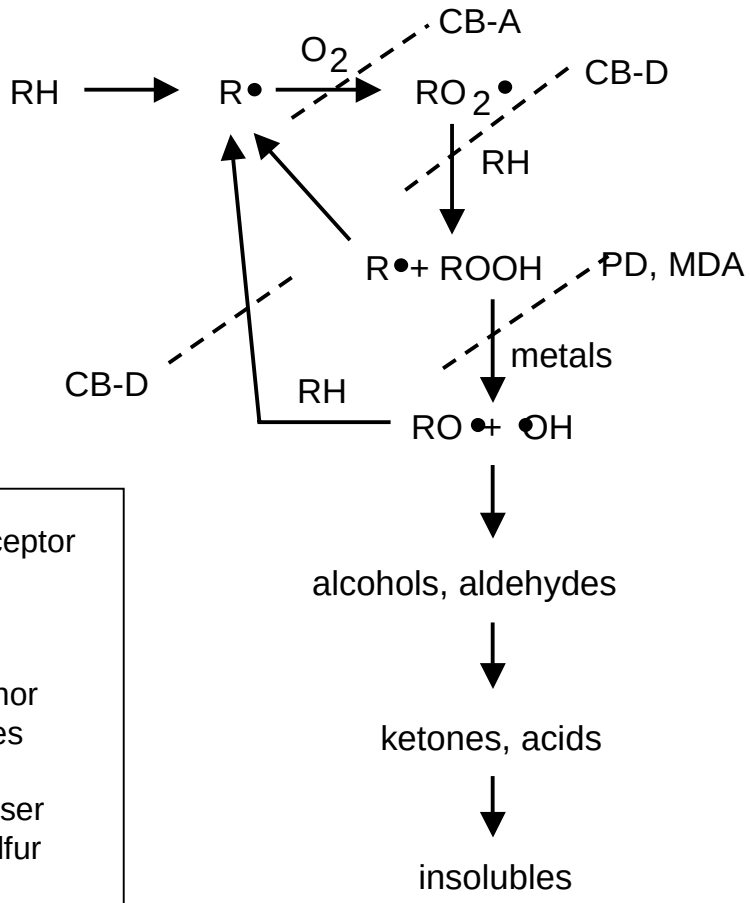
ALBEMARLE

Types Of Fuel



ALBEMARLE

Autoxidation Mechanism
Role of Antioxidants



CB-A = Chain-breaking Acceptor
e.g. quinones, galvinoxyl

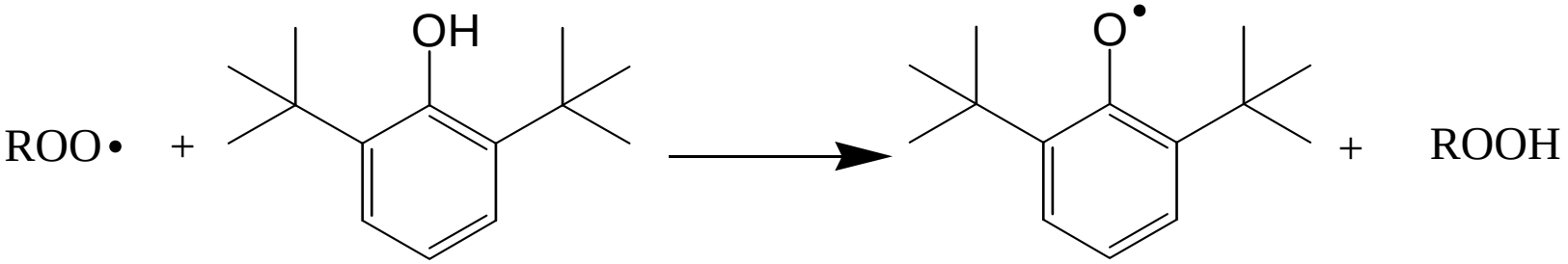
CB-D = Chain-breaking Donor
e.g. phenols, amines

PD = Peroxide Decomposer
e.g. phosphites, sulfur compounds, ZDDP

MDA = Metal Deactivator
e.g. Ethanox 4705

Mechanism Of Antioxidant Function In Fuels

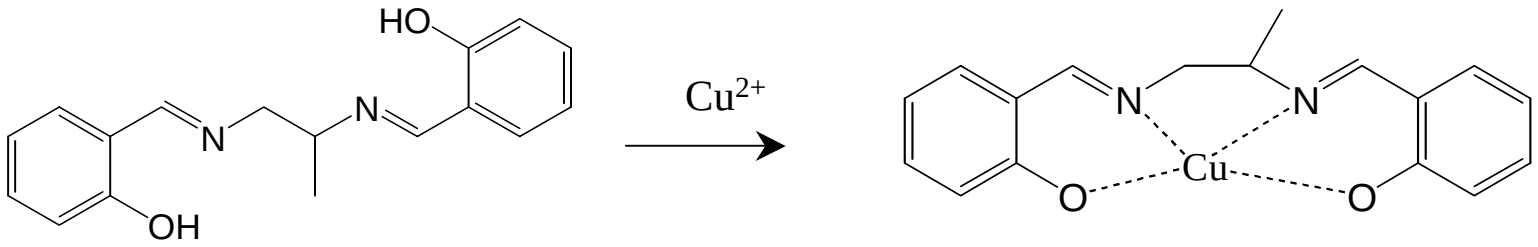
- Primary antioxidant



reactive
peroxy radical

stable
phenoxy radical

- Metal deactivator

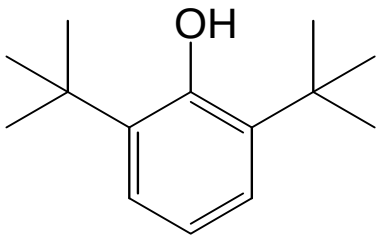


Albemarle's Fuel Antioxidant Products

- Hindered Phenolics
  - Ethanox 4701, Ethanox 4733, Ethanox 4735
  - Ethanox 4737, Ethanox 4545, Ethanox 4775, Ethanox 4776, Ethanox 4778
- Phenylenediamines
  - Ethanox 4720
- Metal Deactivators
  - Ethanox 4705
- Hindered Phenolic / Phenylenediamine Blends
  - Ethanox 4740, Ethanox 4742

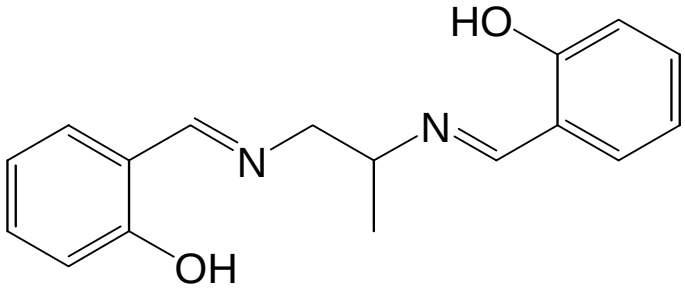
Most Common Albemarle Antioxidants Used In Fuels

- Hindered Phenolics



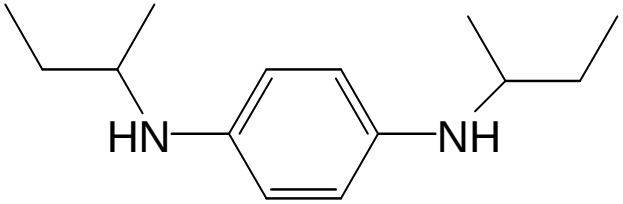
Ethanox 4701, Ethanox 4733

- Metal Deactivators



Ethanox 4705

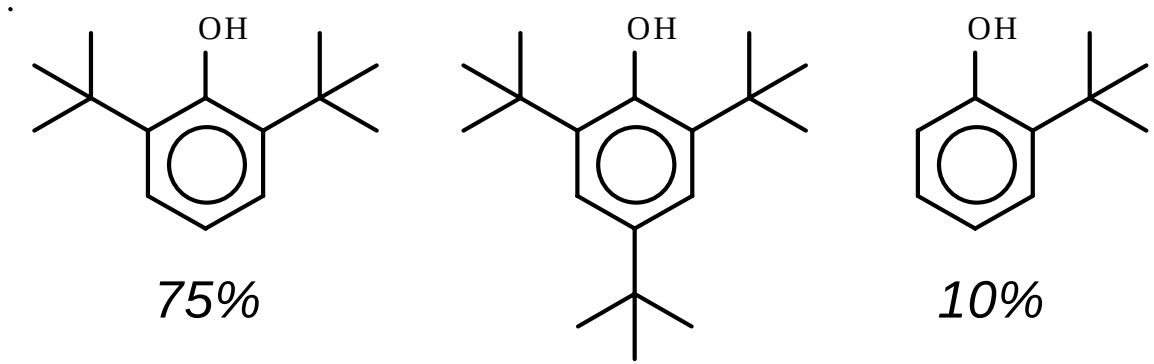
- Phenylenediamines



Ethanox 4720

ALBEMARLE

Ethanox 4733 Antioxidant



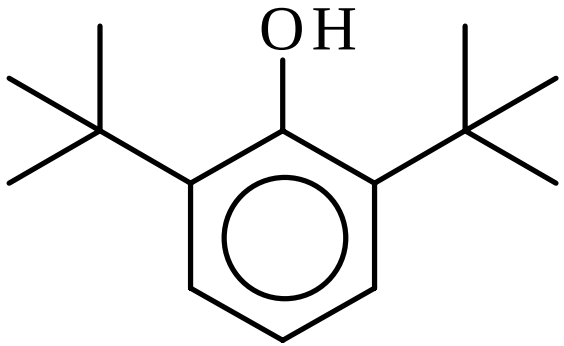
75% *13%* *10%*

Form / Appearance	Clear yellow liquid
Melting Point	17°C*
Viscosity @ 40°C	6.3 cSt
TGA 50% Wt. Loss Temp.	112°C
Uses	Antioxidant for motor and aviation gasolines, jet fuel, diesel fuel, industrial oils.

* Tends to supercool

Ethanox 4701 Antioxidant

www.albemarle.com



> 99+ %

Form / Appearance	Straw to light yellow solid
Melting Point	36°C
Pour Point	--
Viscosity @ 40°C	6.6 cSt
TGA 50% Wt. Loss Temp.	136°C
Uses	Antioxidant for motor and aviation gasolines, jet fuel, diesel fuel, industrial oils

Properties Comparison Between Ethanox 4701 and Ethanox 4733

Property	Ethanox 4701	Ethanox 4733
Activity, %	100	100
Melting Point, ^{o}C	36	17
Viscosity @ 40^{o}C, cSt	6.6	6.3
Flash Point, COC, ^{o}C	92	93
Density @ 20^{o}C, g/mL	0.91	0.94
50% TGA loss temp., ^{o}C	130	136
TTBP, ppm	< 5	130,000

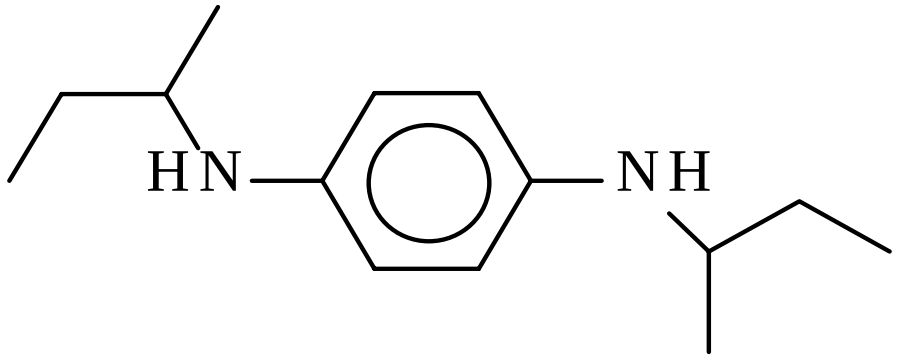
Ethanox 4701 is an excellent replacement for Ethanox 4733 in fuels applications where a TTBP-free antioxidant is required

Ethanox 4701 Versus Ethanox 4733 (Performance)

- Ethanox 4733 has been the fuel antioxidant standard for over three decades because of its lower freeze point
- Both Ethanox 4701 and Ethanox 4733 are 100% active hindered tert-butylphenols
- The fuels industry has generally accepted the interchangeability of Ethanox 4701 and Ethanox 4733

Ethanox 4720 Antioxidant

www.albemarle.com

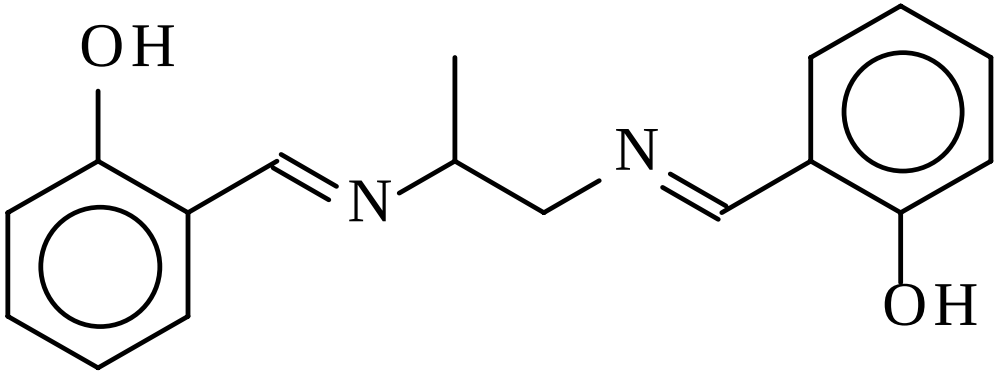


97% min.

Form / Appearance	Brown to red liquid
Melting Point	18°C
Viscosity @ 40°C	11.3 cSt
Uses	Antioxidant for motor gasolines.

Ethanox 4705 Antioxidant

www.albemarle.com



50% active

Form / Appearance	Amber liquid
Viscosity @ 40°C	9.9 cSt
Uses	Antioxidant (metal deactivator) for gasoline, diesel fuel and jet fuel

Fuel Degradation

Gasoline

Reaction of fuel with oxygen to form peroxides and gums. Autoxidation reaction. Catalyzed by some metals.

Peroxides are pro-knocks and can degrade plastic and elastomeric fuel system parts.

Soluble gums can be precursors to engine deposits. Insoluble gums can plug filters.

Degradation inhibited by hindered phenols, phenylenediamines and metal deactivators.

Fuel Degradation

Jet Fuel

Reaction of fuel with oxygen to form peroxides and gums. Autoxidation reaction. Catalyzed by some metals.

Peroxides can degrade plastic and elastomeric fuel system parts.

Soluble gums can be precursors to nozzle and fuel line deposits. Insoluble gums can plug filters.

Degradation inhibited by hindered phenols and metal deactivators.

Jet Fuel Antioxidants

- Hindered Phenol
  - Ethanox 4733, Ethanox 4701
- Metal Deactivator
  - Ethanox 4705

Fuel Degradation

Diesel Fuel and Home Heating Oil

Acid catalyzed combination of certain unstable compounds.

Important in high and low-sulfur diesel fuels and home heating oils.

Inhibited by alkyl amines which neutralize catalyst acids.

Dispersants prevent sedimentation.

Mechanism different in ultra-low sulfur fuels?

Diesel Fuel Antioxidants / Stabilizers

- **Metal Deactivator -** Ethanox 4705
- **Hindered Phenols -** Ethanox 4733, Ethanox 4701

General Fuel AO Recommendations

- Gasoline (motor and aviation)
  - Hindered phenolic, phenylenediamine and metal deactivator
  - Ethanox 4733/4701, Ethanox 4720 and Ethanox 4705
- Jet fuel (turbine)
  - Hindered phenolic and metal deactivator
  - Ethanox 4733/4701 and Ethanox 4705
- Diesel & fuel oils
  - Hindered phenolic and metal deactivator
  - Ethanox 4733/4701 and Ethanox 4705

Performance Comparison In Various Fuels*

Percent reduction in mass of total gum formed compared to fuel with no additive. Fuel aged at 100°C under 100 psig oxygen for 4 hours. All antioxidants added at 25 ppm (v/v).

Ethanox Name	Antioxidant Type	FCC Naphtha 1	FCC Naphtha 2	Visbreaking Naphtha 1	Visbreaking Naphtha 2	Coker Naphtha
4720	PDA	91.7	91.1	37.0	74.7	92.8
4712	BHT	97.2	94.5	79.6	94.6	98.4
4701	DTBP	97.1	88.2	48.7	95.4	99.2

*J. M. Nagpal, G. C. Joshi and S. N. Rastogi, "Stability of Cracked Naphthas From Thermal and Catalytic Processes. Part II. Composition and Effect of Olefinic Structures," Fuel, 74(5), 714 (1995)

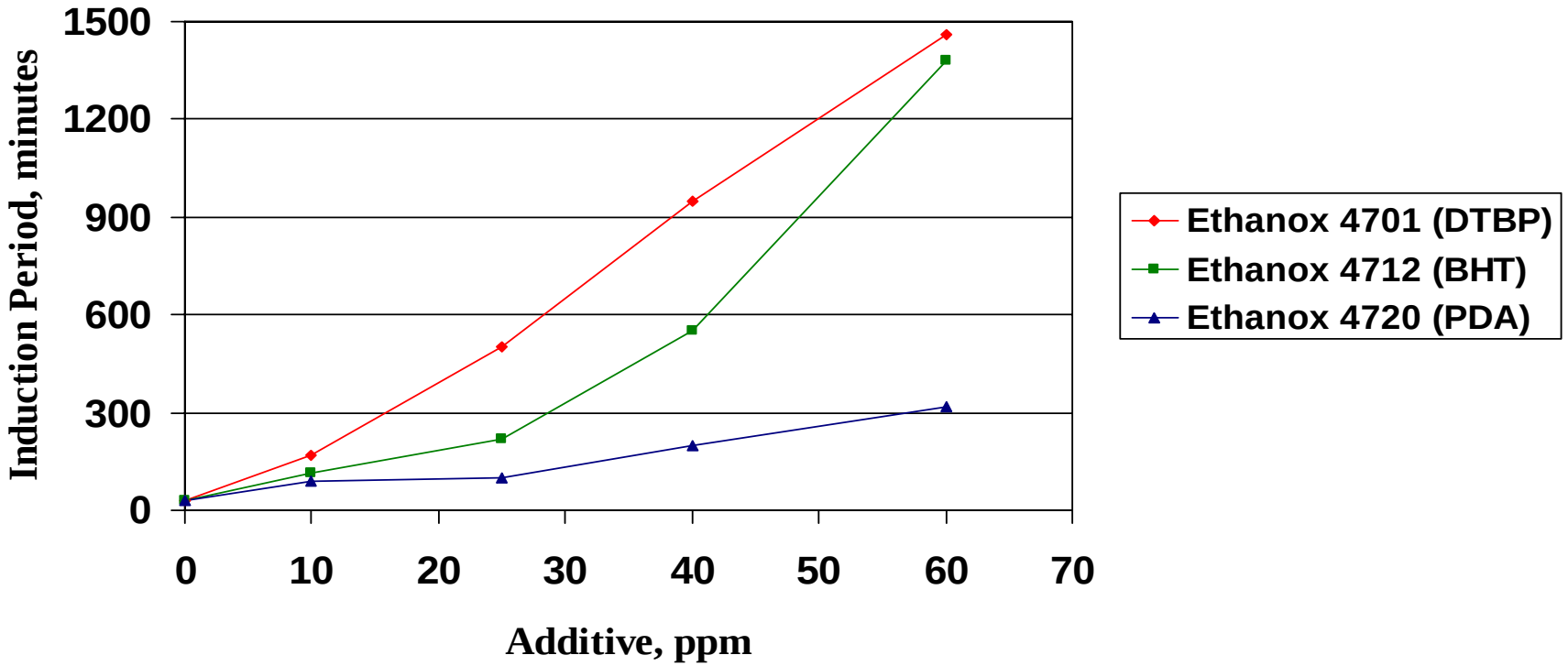
Performance Comparison In Various Fuels*

Percent reduction in mass of total gum formed compared to fuel with no additive. Fuel aged at 43°C at ambient air pressure for 13 weeks. All antioxidants are added at 10 ppm (v/v).

Ethanox Name	Antioxidant Type	FCC Naphtha 1	FCC Naphtha 2	Visbreaking Naphtha 1	Visbreaking Naphtha 2	Coker Naphtha
4720	PDA	26.5	87.2	37.8	24.4	15.5
4712	BHT	95.5	93.1	50.6	94.5	53.8
4701	DTBP	95.2	95.7	78.1	95.8	90.4

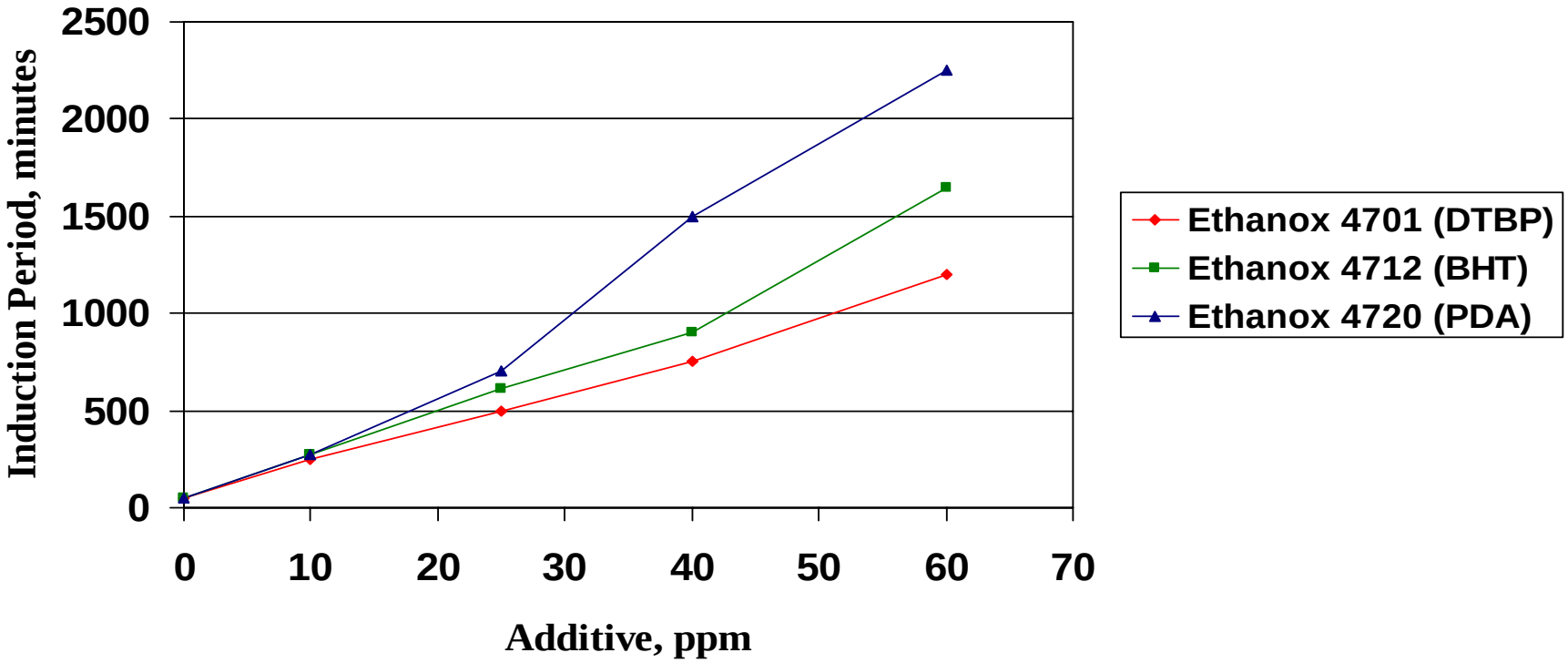
*J. M. Nagpal, G. C. Joshi and S. N. Rastogi, "Stability of Cracked Naphthas From Thermal and Catalytic Processes. Part II. Composition and Effect of Olefinic Structures," Fuel, 74(5), 714 (1995)

Effect of Additives on Induction Period, Visbreaking Naptha



*J. M. Nagpal, G. C. Joshi and S. N. Rastogi, "Stability of Cracked Naphthas From Thermal and Catalytic Processes. Part II. Composition and Effect of Olefinic Structures," Fuel, 74(5), 714 (1995)

Effect of Additives on Induction Period, FCC Naptha A

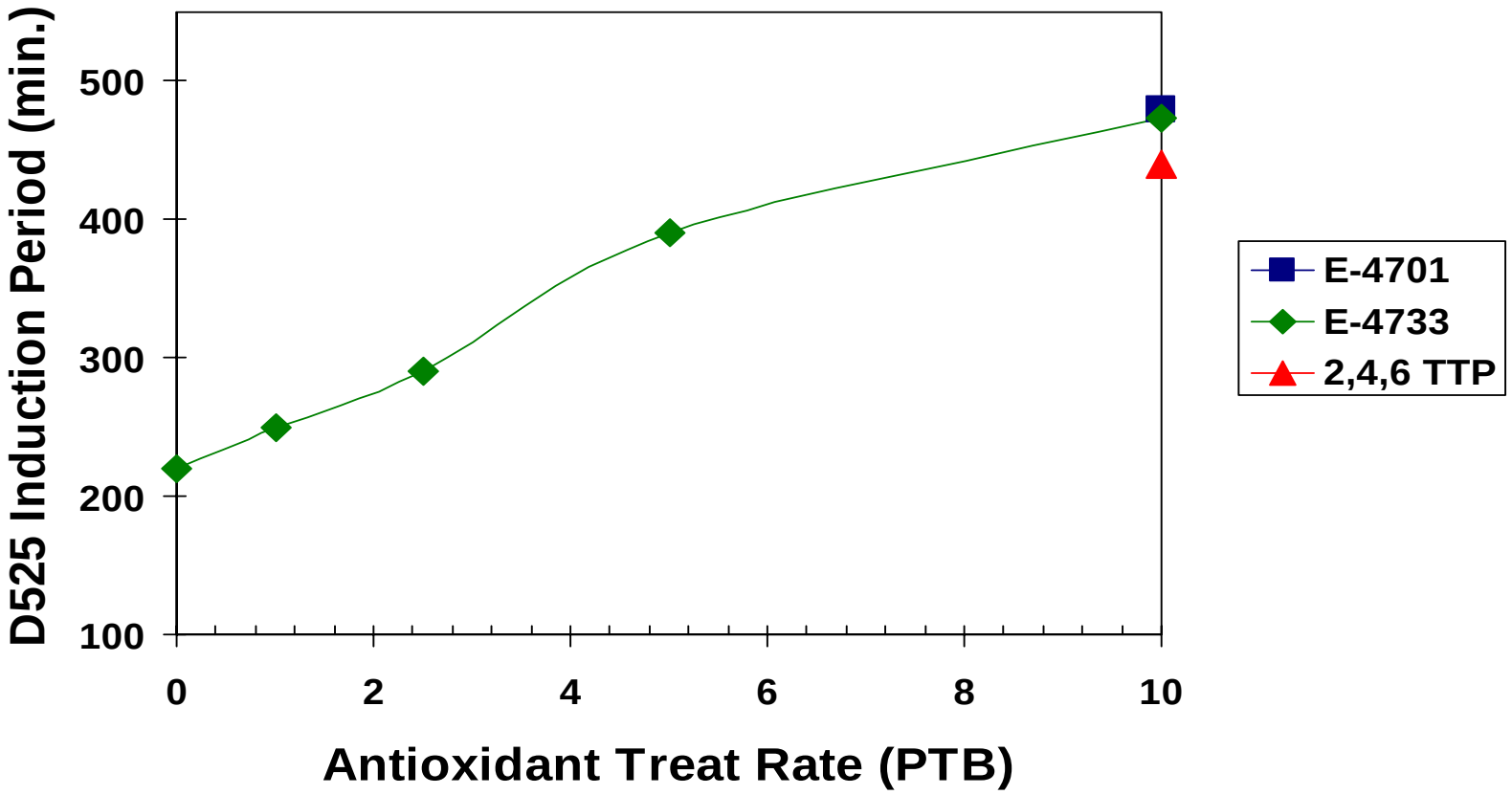


*J. M. Nagpal, G. C. Joshi and S. N. Rastogi, "Stability of Cracked Naphthas From Thermal and Catalytic Processes. Part II. Composition and Effect of Olefinic Structures," Fuel, 74(5), 714 (1995)

ASTM D525 Performance Ethanox 4701 to 4733

www.albemarle.com

Canadian Light Cat Cracked Naphtha



ALBEMARLE

Antioxidant Blend For Gasoline and Jet Fuel

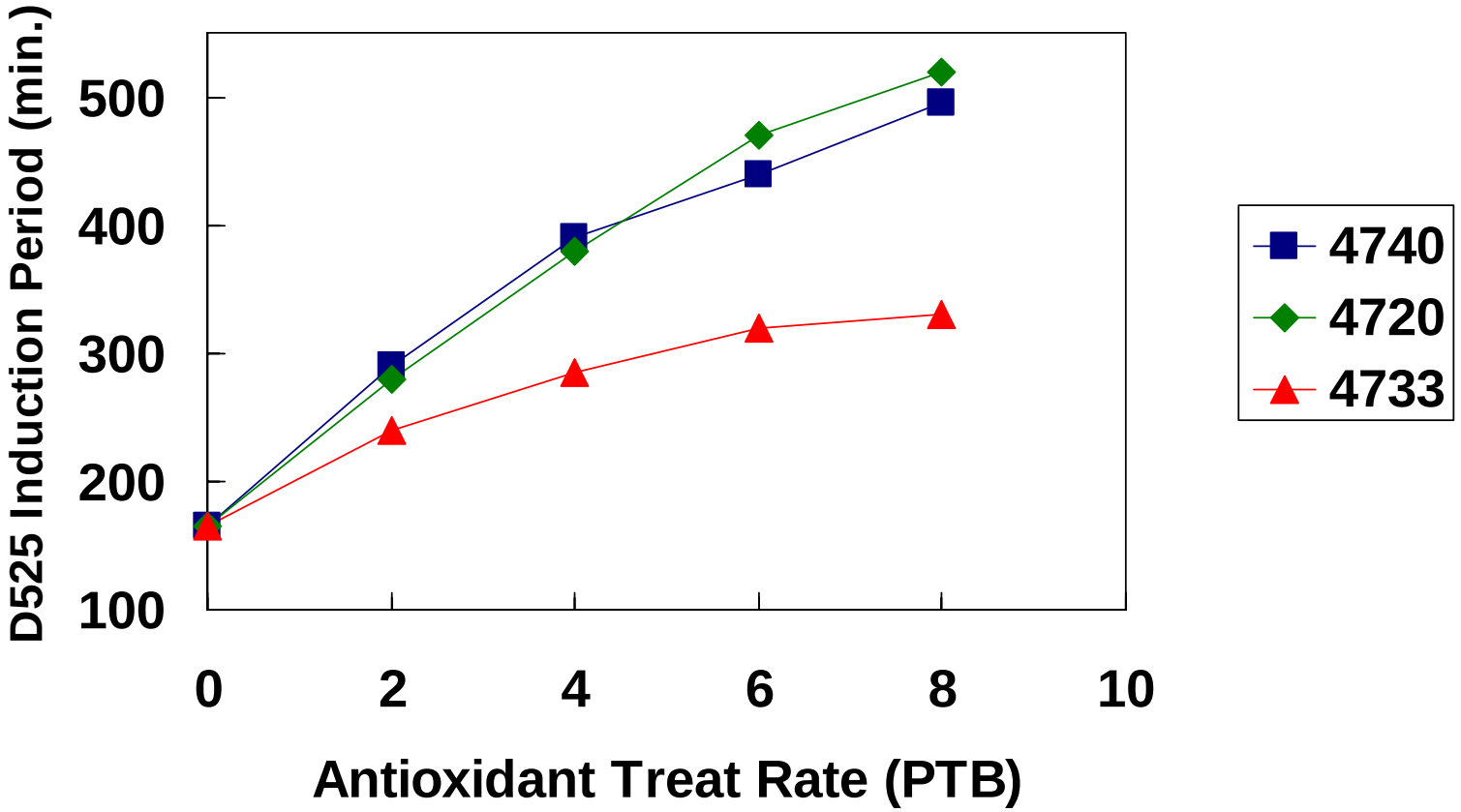
Ethanox 4740

- Low melting point (-14°C).
- Effective in all bench tests.
- Hindered Phenol / PDA synergy.
- Often most cost effective.

ASTM D525 Performance

www.albemarle.com

Cat Cracked Naphtha



ALBEMARLE

Fuel Antioxidant/Stabilizer Use Table

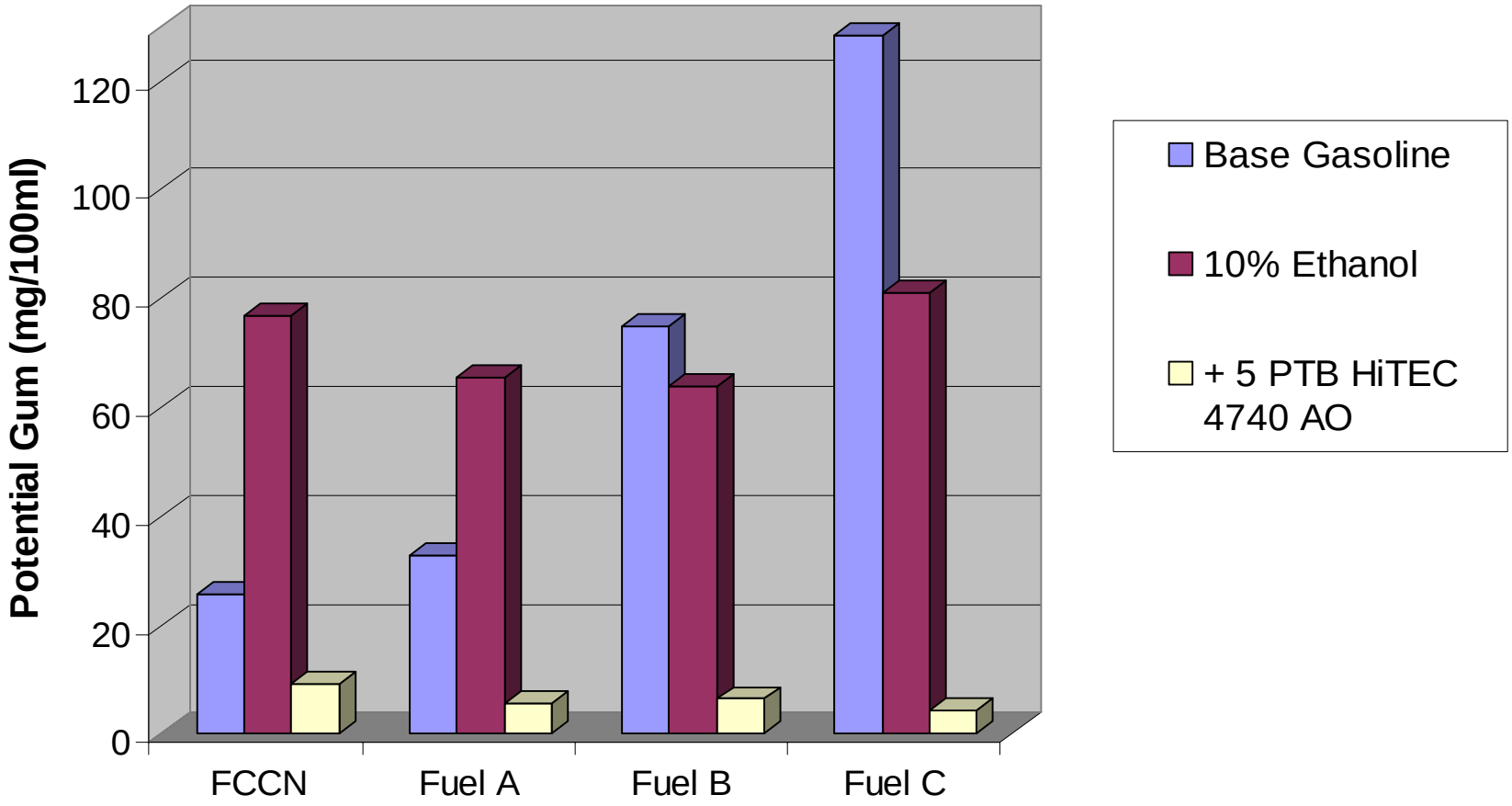
Product Chemistry	Ethanox #(s)	Mainly Used In:
Hindered Phenol	4733	Jet fuels (military and civilian), ultra-low sulfur diesel fuels and relatively stable gasolines.
Phenylenediamine (PDA)	4720	Very unstable gasolines.
Hindered Phenol/ PDA Mixtures	4740	Most gasolines.
Metal Deactivator	4705	Military jet fuels, gasolines and distillate fuels with dissolved metals.
AO Dilutions	Various	Refineries which cannot heat trace additive injection lines. Cold climates.

The Future - More use of Ethanol

- Gasoline
  - Little effect on induction period.
  - Effect on potential gums is fuel dependent.
  - Increases potential for peroxide buildup.

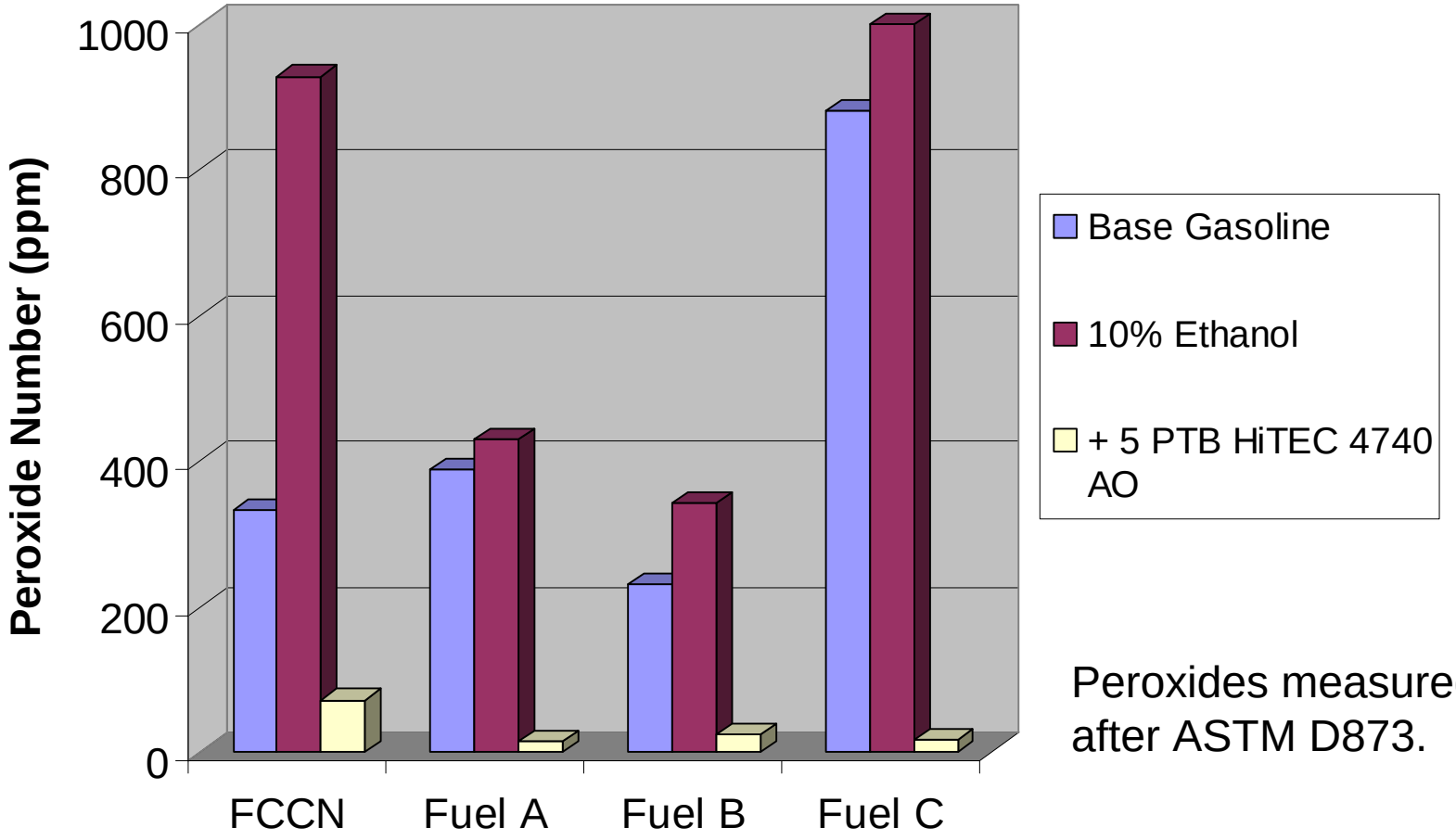
Effect of Ethanol on Potential Gum

4-Hour ASTM D873



ALBEMARLE

Effect of Ethanol on Peroxide Formation

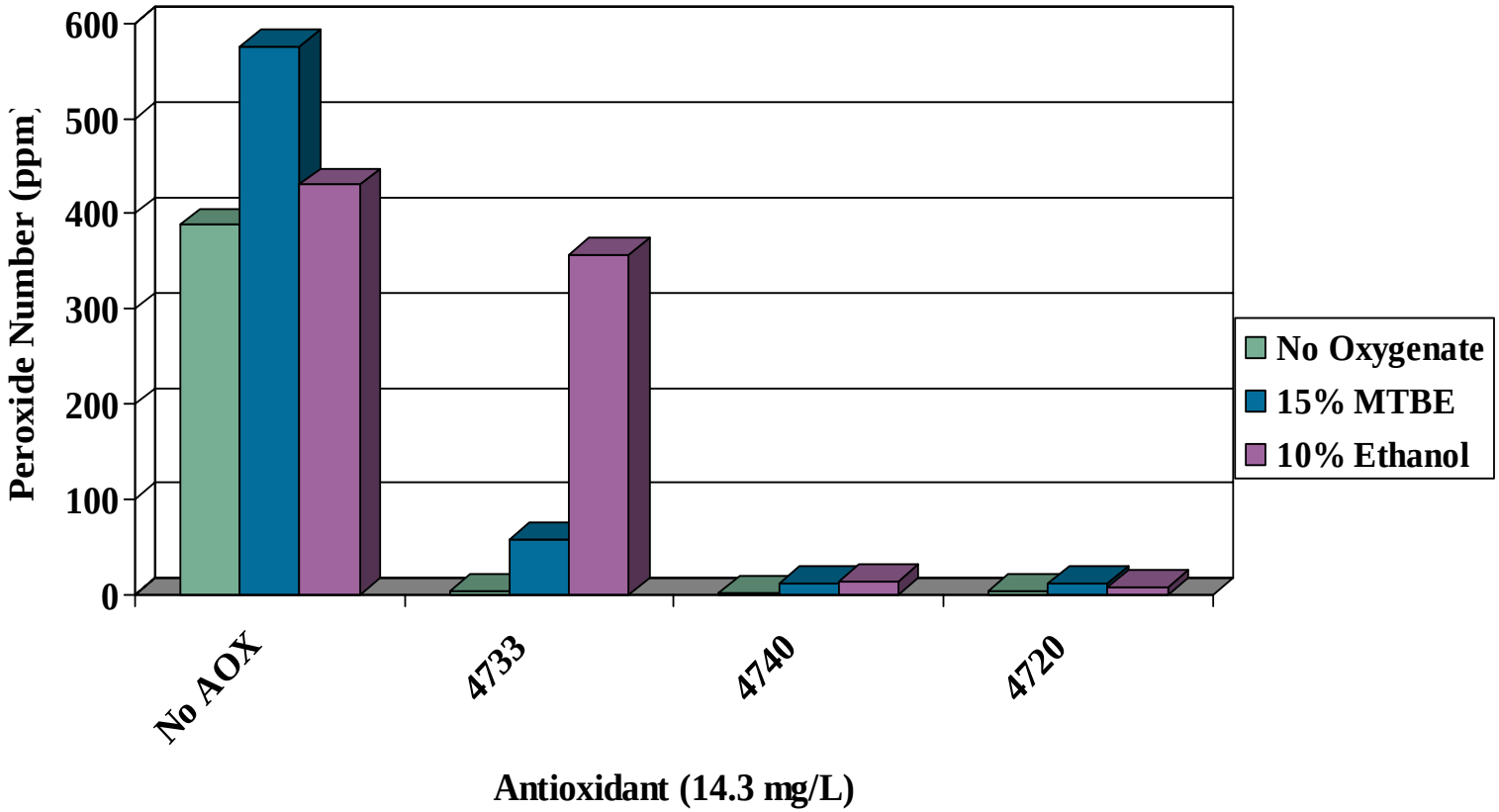


Peroxides measured after ASTM D873.

ALBEMARLE

Effect of Antioxidants and Oxygenates On Peroxide Formation in ASTM D 873

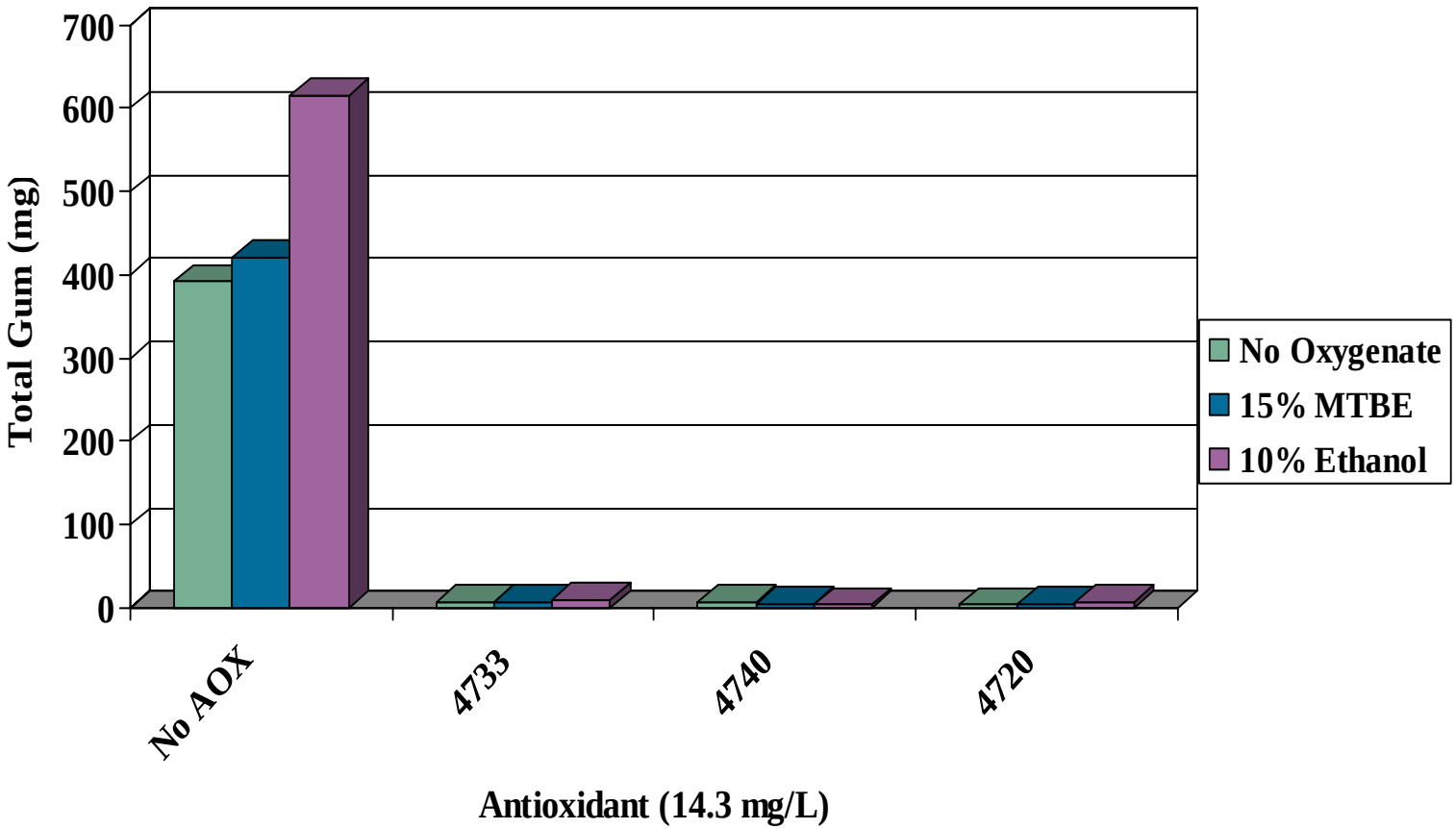
Testing Performed In Unleaded Gasoline, 100 psi O_2, 100°C, 4 hours aging



ALBEMARLE

Effect of Antioxidants and Oxygenates On Storage Stability in ASTM D 4625

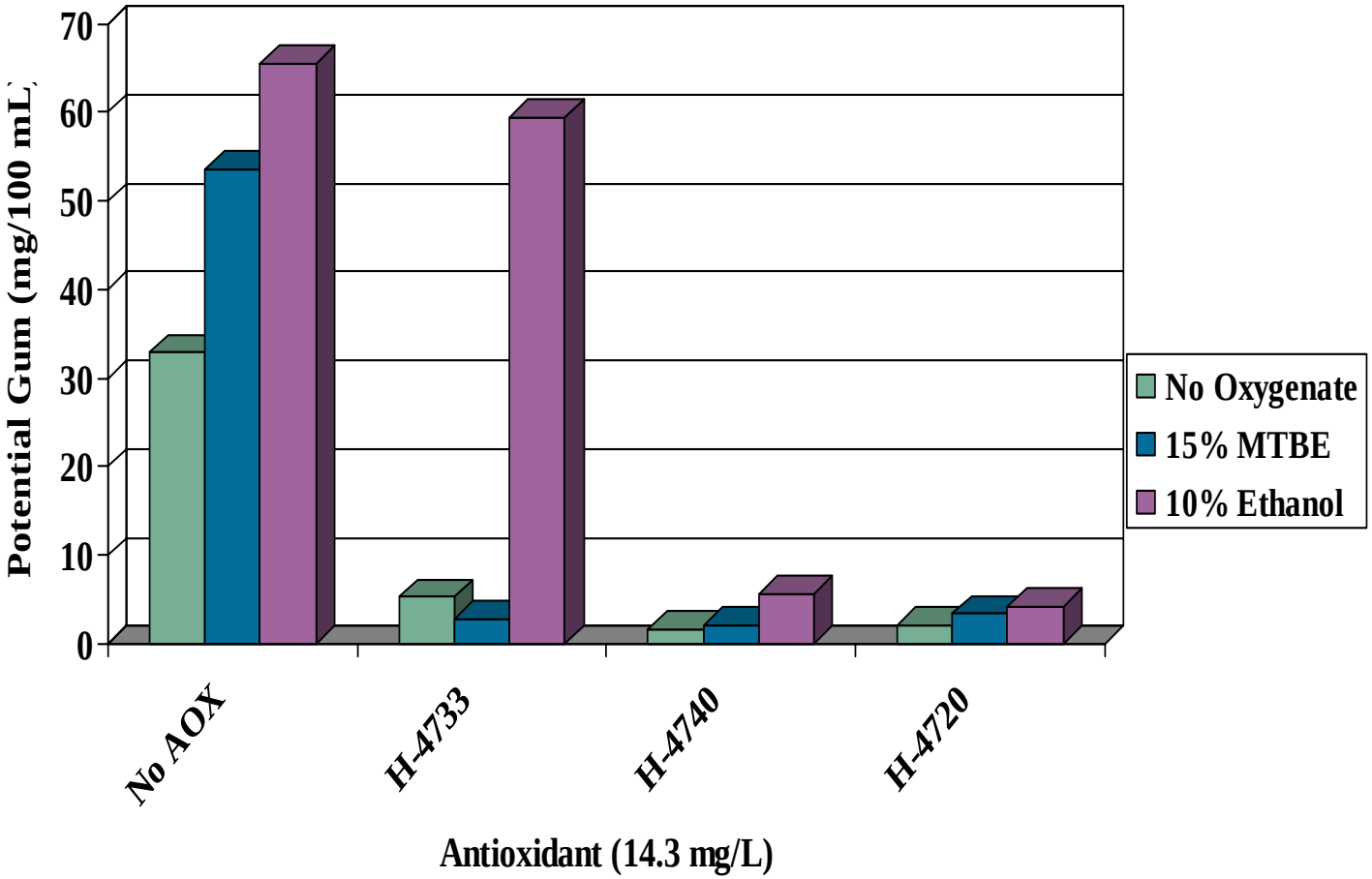
Testing Performed In Unleaded Gasoline, 43°C, 13 weeks aging



ALBEMARLE

Effect of Antioxidants and Oxygenates On ASTM D 873 Performance

Testing Performed In Unleaded Gasoline, 100 psi O_2, 100°C, 4 hours aging

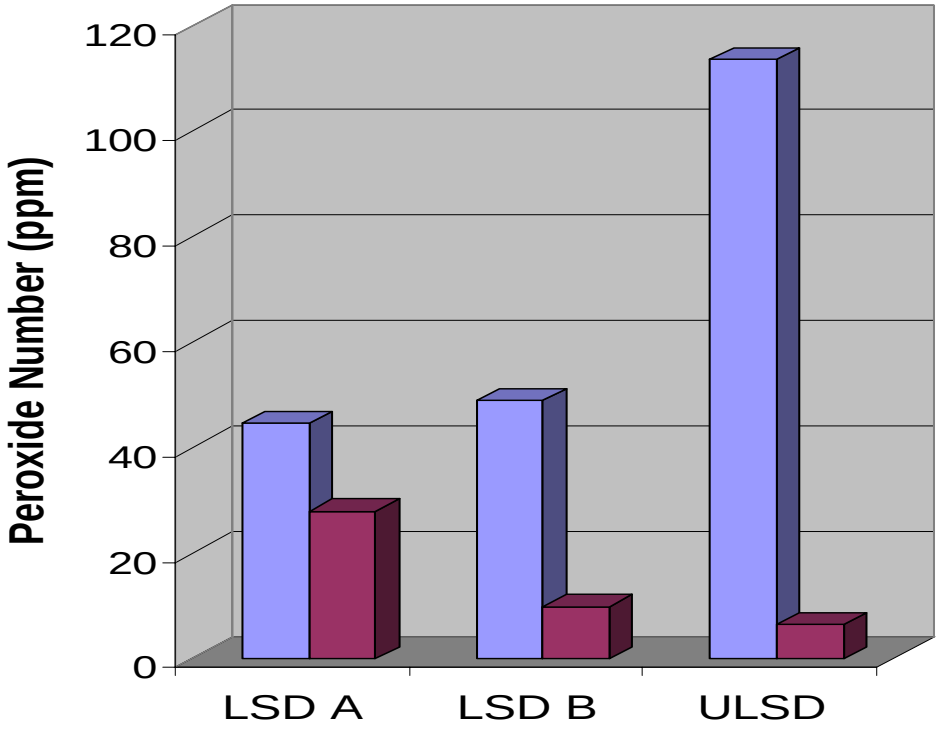


ALBEMARLE

The Future - Sulfur Reduction

- **Gasoline**
  - Increases induction period.
  - Decreases potential gums.
  - May increase potential for peroxide buildup.
- **Diesel Fuel**
  - Increases storage and thermal stability (resistance to sediment formation).
  - May increase potential for peroxide buildup.

Peroxide Formation in ULSD



Peroxides measured after ASTM D6468.

ALBEMARLE

Antioxidants For Fuel Applications

Albemarle Corporation
Baton Rouge, LA 70820 USA

Vince Gatto
225-768-5656
FAX 225-768-5607
vince_gatto@albemarle.com

Albemarle Europe SPRL
Louvain-la Neuve, Belgium

Didier De Schampheleer
32 10 48 1772
FAX 32 10 48 3921
didier.de.schampheleer@albemarle.com

ALBEMARLE