

# SUSTAINABLE CHEMISTRY CATALYST

## Collaborative Innovation Forum Functional Substitutes to 6PPD in Tires

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Lowell Center for Sustainable Production  
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[www.uml.edu](http://www.uml.edu) | [www.sustainableproduction.org](http://www.sustainableproduction.org)

Highline College Des Moines, WA  
Dec. 14, 2022

IP Landscape review

Miles Dearth, Esq.

# Search Approaches

Tools: Google Patent  
PatBase®

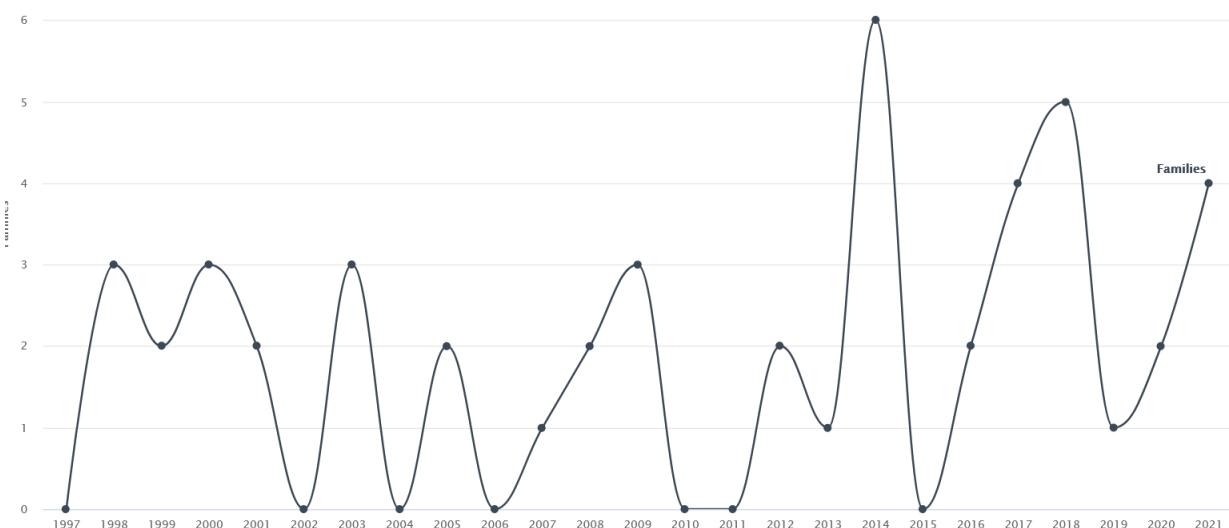
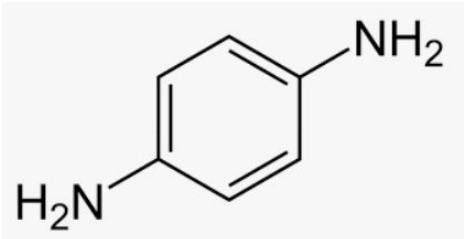


- By Keywords
- Contextual – large block of text
- cross w/ Assignees
- cross w/ classification
- cross w/ inventor (author)
  - Literature-to-patents
- By chemical fragment (ACS SciFinder®)
- Text and Data Mining (ACS)

# Top- Down Keywords

p-phenylenediamine and tire

116 families



Goodyear Co. (28)

Bridgestone Corp. (20)

Firestone Tire And Rubber Co. (16)

Toyo Tire And Rubber Co. Ltd. (8)

Hankook Tire Co. Ltd. (6)

Triangle Tire Co. Ltd. (6)

Hankook Tire MFG Co. Ltd. (4)

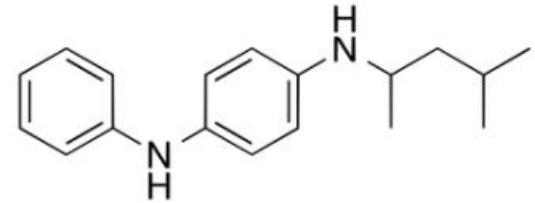
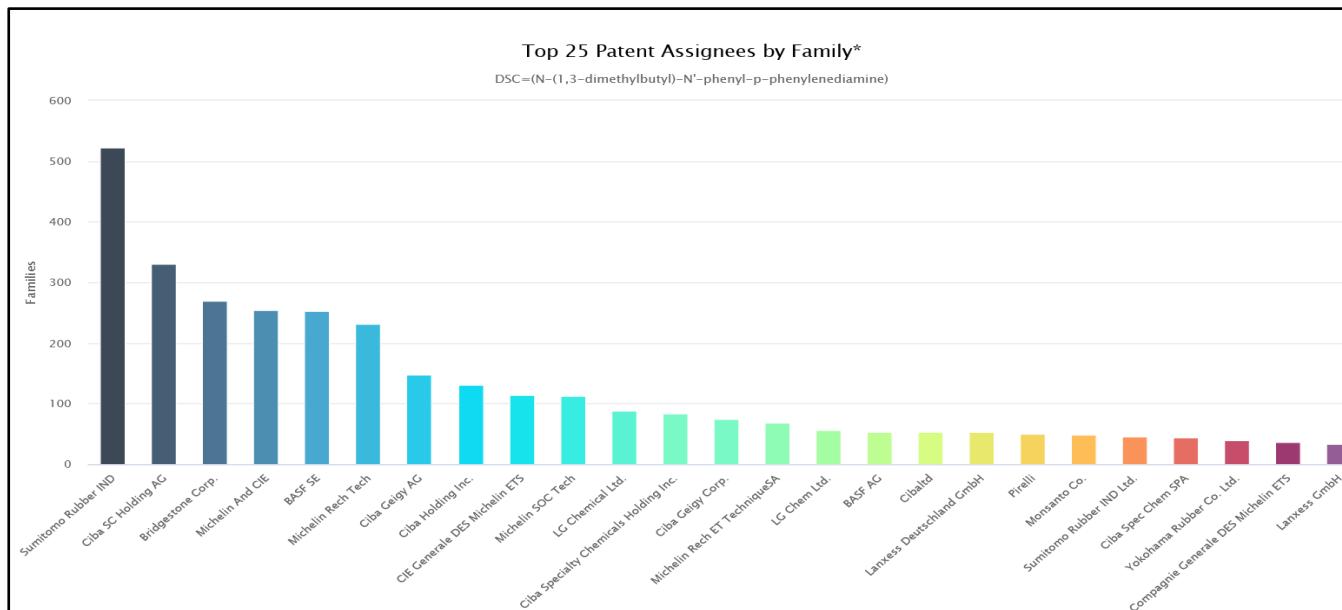
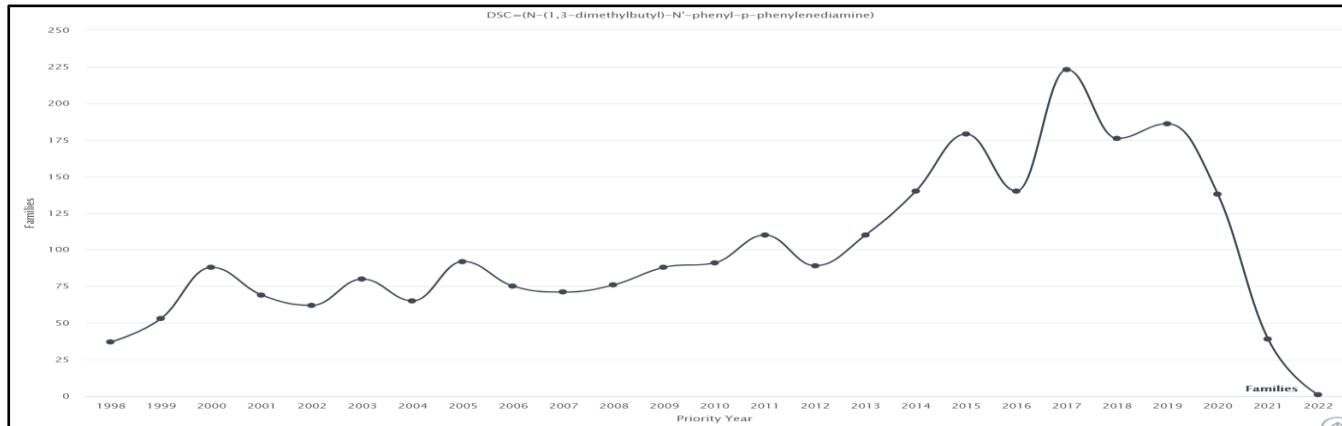
Ohtsu Tire And Rubber Co. Ltd. (4)

Kumho Tire Co. Inc. (3)

Shandong Linglong Tyre Co. Ltd. (3)

# Top- Down Keywords

N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine



2867 Families

	Patent Assignee	Families
<input type="checkbox"/>	Sumitomo Rubber IND	522
<input type="checkbox"/>	Ciba SC Holding AG	331
<input type="checkbox"/>	Bridgestone Corp.	269
<input type="checkbox"/>	Michelin And CIE	254
<input type="checkbox"/>	BASF SE	253
<input type="checkbox"/>	Michelin Rech Tech	231
<input type="checkbox"/>	Ciba Geigy AG	148
<input type="checkbox"/>	Ciba Holding Inc.	131
<input type="checkbox"/>	CIE Generale DES Michelin ETS	114
<input type="checkbox"/>	Michelin SOC Tech	112
<input type="checkbox"/>	LG Chemical Ltd.	88
<input type="checkbox"/>	Ciba Specialty Chemicals Holding Inc.	84
<input type="checkbox"/>	Ciba Geigy Corp.	74
<input type="checkbox"/>	Michelin Rech ET TechniqueSA	69
<input type="checkbox"/>	LG Chem Ltd.	57
<input type="checkbox"/>	BASF AG	54
<input type="checkbox"/>	Cibaltd	54
<input type="checkbox"/>	Lanxess Deutschland GmbH	54
<input type="checkbox"/>	Pirelli	50
<input type="checkbox"/>	Monsanto Co.	48
<input type="checkbox"/>	Sumitomo Rubber IND Ltd.	46
<input type="checkbox"/>	Ciba Spec Chem SPA	44
<input type="checkbox"/>	Yokohama Rubber Co. Ltd.	40

...and “tread”

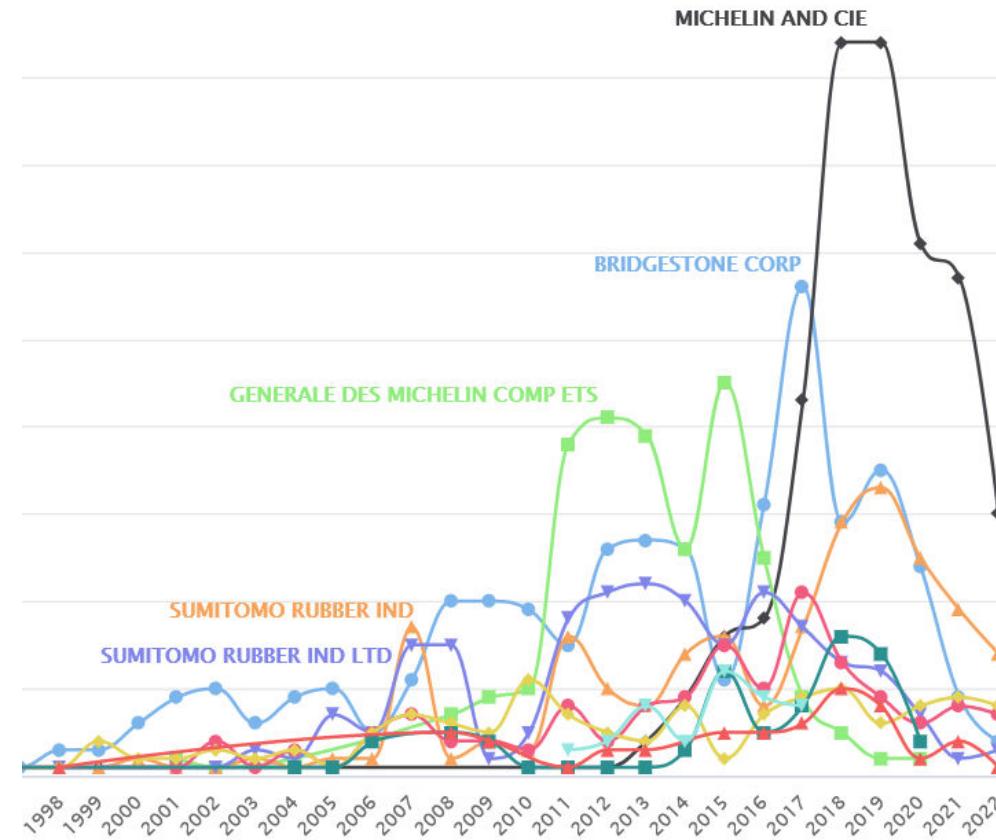
1506 Families

...

...and “ozone”

496 Families

- BASF SE (115)
- Bridgestone Corp. (109)
- Sumitomo Rubber IND Ltd. (107)
- Michelin And CIE (102)
- Generale DES Michelin Comp ETS (77)
- Sumitomo Rubber IND (73)
- Goodyear Co. (58)
- Zeon Corp. (53)
- Mitsui Chemicals Inc. (44)
- Arlanxeo Deutschland GmbH (38)



..... And Toxic\*

45 Families

# Review of Hits

## 1. Derivatives of PPD

a. oxyalkylated carbonyl Salts	Pirelli	10 759 227	Active
b. Stearyl	Flexsys BV	US 6 444 759	Expired
c. quinone diamine	Flexsys BV	US 5 959 126	Expired
d. mono-oxalate *	Uniroyal	US 2 632 770	Expired
e. thiomethyl sub.	BASF	US 7 799 951	Expired

## 2. Coupling with diol

Flexsys      10 160 718      Active

## 3. Coupling with carbonyls

Si Group      US 6,706,216      Expired

## 4. Aldehyde condensates

Toto Ltd      5 280 071      Expired

## 5. hydroxylated or quinonimine

Michelin      WO2022146441 Pending

\* **purported reduced toxicity (1952)**

# Review of Hits cont.

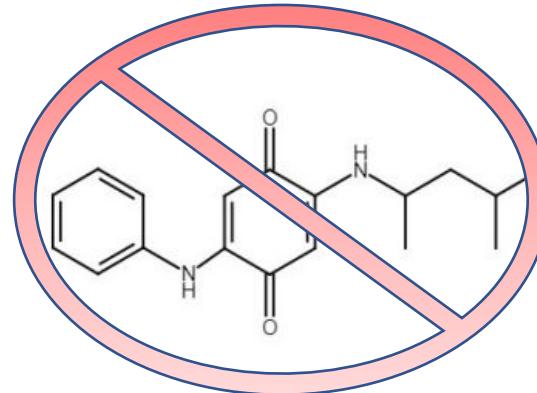
## Increased efficiency / permanence / synergism / non-PPD compounds

1. Blends of PPD species	Bridgestone	2022/0243041 A1	Pending
2. Synergistic blends	Univ. Oil	FR2105563	Expired
3. Synergist blends			
1. 6-PPD and para-di(nitroso)benzene	Bridgestone	US 4 568 711	Expired
4. 6-anilino-2,2,4-trimethyl-1,2-dihydroquinoline or 6-anilino-2,2,4-trimethyl-1,2,3,4-tetrahydroquinoline	BFGoodrich	US 3 362 930	Expired
5. Slower migration and no PPD quinone forms	Michelin	WO2022146441	Pending
6. para-phenylenediamine + dihydroquinoline	Continental	US2022259413	Pending
7. Methylene acceptor / donor in-situ	Michelin	US 9 708 459	Active
8. Phosphnitrilic antiozonants	Firestone	US 3 474 052	Expired

WO22146441

Title: RUBBER COMPOSITION WITH LONGER LASTING ANTIOZONATION

Assignee: Michelin & Cie



Published in: [Family Explorer](#)

Country	Publication number	Publication date	Application number	Application date	Description
WIPO (P.C.T)	<a href="#">WO22146441 A1</a>	Claims   Description Jul 7, 2022	WO2020US67658	Dec 31, 2020	Publication of internationa...

Owner(s) / Assignee(s): MICHELIN AND CIE; GENERALE DES MICHELIN COMP ETS

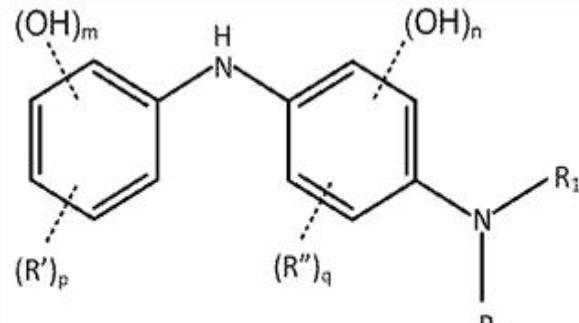
Inventor(s): ARNOLD JESSE J; SALIT ANNE FREDERIQUE; YANG XIAOFENG SHAW

Priority: [WO2020US67658](#) 20201231

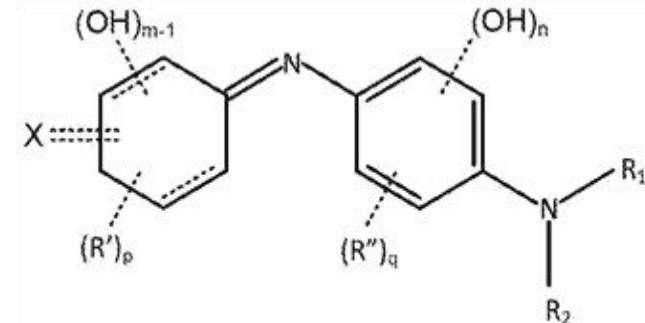
Classifications: International (IPC) [C08K5/18](#) [C09C1/44](#) [C09C1/56](#) (Core/Invention)  
Cooperative (CPC) [B60C1/00](#) [B60C1/0025](#) [B60C2001/005](#) [C01P2002/86](#) [C01P2006/12](#) [C08K3/04](#) [C08K3/06](#) [C08K5/18](#) [C09C1/44](#) [C09C1/46](#) [C09C1/56](#)

Cited documents: [WO17112440 A1](#), [WO07042418 A2](#), [US8101679 BB](#), [US2015252167 AA](#), [US2015031810 AA](#),

- Abstract: A rubber composition having improved antiozonation performance
- substituted hydroxyl-phenyl-p-(hydroxy)phenylenediamine.
- long lasting antiozonation performance, slowing migration through the rubber article
- reducing effluence of the antiozonant.
- continuous and intermittent dynamic operation conditions and require protection from ozonation.



(I)

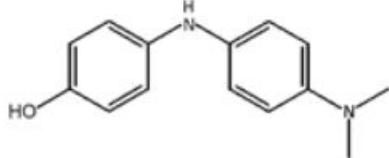


(II)

# Examples WO2022146441

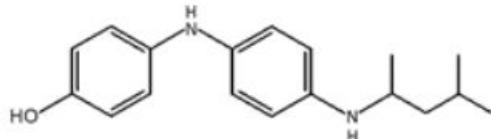
## Group I hydroxyl substitution

4-((4-(dimethylamino)phenyl)amino)phenol- (I-a);



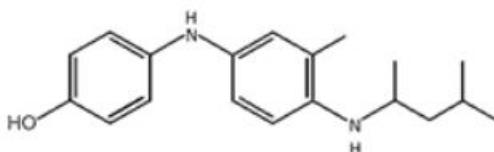
(I-a)

4-((4-((4-methylpentan-2-yl)amino)phenyl)amino)phenol (I-b);



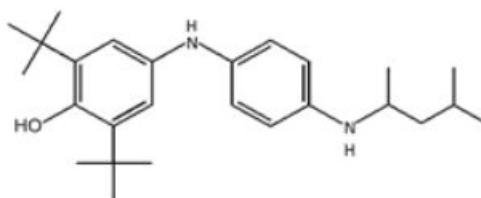
(I-b)

4-((3-methyl-4-((4-methylpentan-2-yl)amino)phenyl)amino)phenol (I-c);



(I-c)

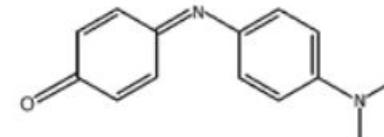
2,6-di-tert-butyl-4-((4-((4-methylpentan-2-yl)amino)phenyl)amino)phenol (I-d);



(I-d)

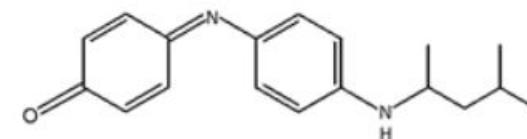
## Group II quinoneimines

4-((4-(dimethylamino)phenyl)imino)cyclohexa-2,5-dienone;



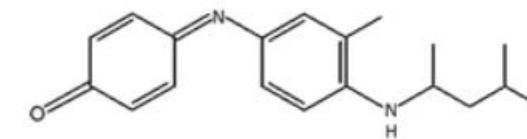
(III-a)

4-((4-((4-methylpentan-2-yl)amino)phenyl)imino)cyclohexa-2,5-dien-1-one;



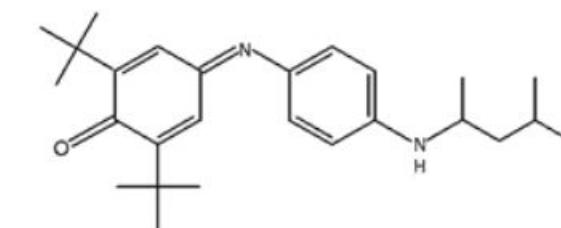
(II-b)

4-((3-methyl-4-((4-methylpentan-2-yl)amino)phenyl)imino)cyclohexa-2,5-dien-1-one;



(II-c)

2,6-di-tert-butyl-4-((4-((4-methylpentan-2-yl)amino)phenyl)imino)cyclohexa-2,5-dien-1-one;



(II-d)

# Summarizing

- Powerful Web-based tools to filter IP landscapes
- Combination of search approaches
- Review forms Insight
  - History of problem-solutions;
  - New problem-solutions emerging;
  - Follow Hits forward to present;
  - Freedom to practice
- Moving the frontier:
  - It takes a team

# Thank you



***Miles Dearth, Esq.***

- 30+ years in the chemical and polymer industries including mfg., commercial development and IP legal roles;
- BFGoodrich, Clariant, Parker Lord, and Celanese
- BS/BA (BioPhysics/Organic Chemistry) The Ohio State Univ.
- MBA-Marketing The Ohio State Univ.
- J.D. Cleveland State University;
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- [Miles.dearth@ace-laboratories.com](mailto:Miles.dearth@ace-laboratories.com)

