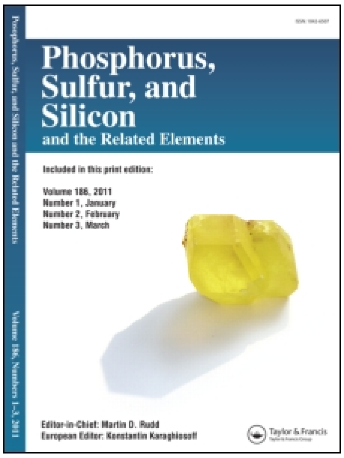

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RECENT INDUSTRIAL ORGANOSULFUR CHEMISTRY

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RECENT INDUSTRIAL ORGANOSULFUR CHEMISTRY

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Abstract This review includes new developments in aromatic sulfide and sulfone thermoplastics, electroconductive and electrooptical polymers, polymeric sulfur cements and coatings, sulfonated polymers, and rubber vulcanizing agents. New agrochemicals include sulfonylurea herbicides, and tetrathiocarbonate soil fumigants. A new cardiac drug is based on phenothiazine. Other recent developments include oil additives, ligands, surfactants, dye processes, textile finishes, and personal care products.

INTRODUCTION

This survey covers a range of topics showing the broad industrial applicability of organic sulfur chemistry.

SULFUR-BASED POLYMERS

Sulfur-containing polymers were surveyed very thoroughly by Duda and Penczek in an encyclopedia article published in 1989.[1] In the present review, special attention will be given to the aromatic polymers with sulfur in the backbone, which are becoming increasingly important as engineering thermoplastics.

Sulfide Polymers

Polyphenylene sulfide is now used on a large scale for electrical and automotive parts in view of its good electrical properties, reasonably high heat distortion temperature, high strength especially when reinforced, chemical resistance and inherent flame resistance. Reviews on polyphenylene sulfide have recently been published[2-5] and production figures are available.[6] Polyphenylene sulfide is made by the displacement of both chlorine atoms of p-dichlorobenzene by sodium sulfide in a dipolar aprotic solvent. The reaction mechanism is not without controversy - there is some arguable evidence that it may actually involve radical ions.[4]

The earliest commercial polyphenylene sulfides were not of very high molecular weight. One method to increase molecular weight is to allow some crosslinking by holding the polymer under air at elevated temperatures. A recent study shows the formation of new sulfide linkages and ether linkages.[7] Chain extension and branching probably both occur.

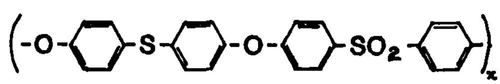
Phillips has found that by having an alkali metal carboxylate present during the nucleophilic displacement step, higher molecular weight linear polymer is obtained.[3] Kureha found that by completing the reaction in a two-phase reaction mixture, a linear high molecular weight polyphenylene sulfide could be made.[8] Bayer has claimed that use of dimethylacetamide or anhydrous N-methylcaprolactam as solvent gives higher molecular weight.[8a]

While the chemistry used industrially for polyphenylene sulfide continues to be the original reaction of sodium sulfide with p-dichlorobenzene, a sulfide contaminated brine is produced as a byproduct and it is also difficult to remove all traces of sodium chloride from the polymer. Eastman has a series of recent patents on a route to polyphenylene sulfides containing a small fraction of disulfide linkages by the reaction of p-iodobenzene with sulfur, with recovery of the iodine.[8b] Tsuchida recently reported new synthetic routes in which diphenyl disulfide or thiophenol is polymerized by Lewis acids or by various oxidative routes, including catalytic air oxidation in the presence of a vanadium catalyst.[9] It is not yet evident whether high molecular weight polymer can be made by Tsuchida's processes.

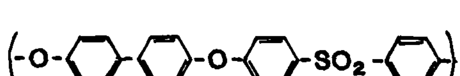
Structural modifications of the polyphenylene sulfides continue to appear. Phillips, Kureha and Tosoh have described polyphenylene sulfide-ketones,[10a-c] and the recent product of this class introduced by Tosoh is said to have a 350°C heat deflection temperature when glass-filled.[10d]

Sulfone Polymers

The aromatic polysulfones tend to have very high glass-transition temperatures. The most familiar and oldest commercial example is the polysulfone from bis(4-chlorophenyl) sulfone and bisphenol A.[11] used especially for electrical and automotive applications. Hybrids between the sulfide and sulfone polymers were first disclosed by Phillips in 1977 but have just recently been commercially introduced as Phillips' RYTON S series.[6a]

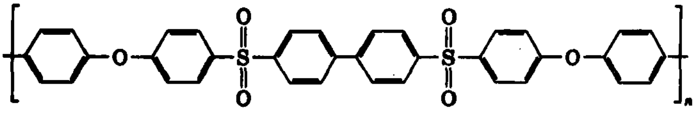


By reaction of 4,4'-dihydroxydiphenyl, which has recently become commercial, with bis(4-chlorophenyl) sulfone, a polysulfone with enhanced high temperature properties can be produced, Amoco's RADEL R.[12,13]



ICI has been developing new polysulfones with good solvent resistance but even higher glass transition temperatures than their polyether sulfone VICTREX PES. By copolycondensation reactions, a variety of aromatic structures have been introduced into the backbone of the polysulfone, such as p-terphenylene and phenylenebis-sulfone units.[14] Asahi Glass has developed a polysulfone-ether-sulfide with improved impact, heat distortion temperature and processing.[14a]

A new synthetic approach to condensation polymers with aromatic backbones has been revealed recently by Union Carbide.[15] With a Ni^0 catalyst, zinc metal will effect reductive coupling of chloroaromatic compounds without the need for the chlorine to be activated. With bis(chlorophenyl) intermediates, such as bis(4-chlorophenoxyphenyl) sulfone, polymers otherwise difficult to prepare can be made, such as the following;



Conductive Thiophene Polymers

Sulfur-based polymers are being evaluated in conductive polymer applications and in the newly-initiated field of optical computers.

It was found by Elsenbaumer at Allied Signal that 3-alkylthiophenes could be converted to conductive polythiophenes with much improved polymer properties.[16] One such polymer, poly-3-octylthiophene, is offered on a development basis by the Neste company (Finland) in admixture with polyvinyl acetate, as a conductive film.[17] Elsenbaumer and others have shown that strong acids can be used for doping such conductive polymers; self-doping polythiophenes with sulfonic acid groups attached covalently to the polymer chain[18] or generated during the polymerization are under investigation.[19]

By cocondensing bithienyls with benzaldehyde, a family of conductive polymers with nonlinear optical properties has been prepared.[20,21] These appear to be promising as switching elements for optical computer circuits, which in theory could be orders of magnitude faster than computers using electron conduction. This work is still in the laboratory but has attracted industrial support.

<u>Sulfur Cement and Plasticized Sulfur</u>

Potentially large tonnages of sulfur might be used in the form of a condensation polymer of sulfur with dicyclopentadiene and higher cyclopentadiene Diels-Alder oligomers (a cheap petrochemical byproduct) to make "sulfur cement".[22,23] The structure of this polymer is not known in detail but apparently consists of cyclopentene rings linked by polysulfide chains.[23a] Recently reported tests show that sulfur cement (as sulfur concrete) in construction of chemically-resistant floors, walls and foundations gives better long term chemical resistance than concrete based on portland cement. Sulfur concrete has unusual resistance to acids and salt environments. Recently sulfur cement has been shown by work in the US and Holland to be very useful for leach resistent encapsulation of low level radioactive and toxic metal-containing wastes.[23b-d]

Recent progress has been made by researchers at the O. M. Scott & Sons Co. in the U. S. on use of sulfur plasticized by bis(butoxycarbonylethyl) polysulfide as a fertilizer coating.[24]

<u>Sulfonated Polymers</u>

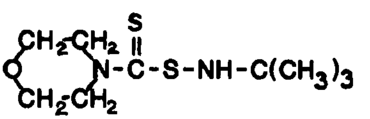
Exxon has shown that sulfonation of polystyrene or EPDM by acetylsulfate gives a highly controllable reaction with uniform sulfonation.[25] Zinc salts of EPDM sulfonates form strong heat-stable complexes with a styrene-vinylpyridine copolymer. Such complexes can be used at low concentrations in hydrocarbon-based drilling fluids to form a gel strong enough to suspend rock chips, yet able to pass through a filter.

Recent research at Dow has led to a process for controlled surface sulfonation of a variety of polymers by SO_3 in an inert carrier. Medical plastics which can bind heparin and which prevent blood clotting can thus be made.[25a]

RUBBER CHEMICALS

A great deal of toxicological concern has been expressed recently regarding nitrosamines formed in rubber products from the secondary amine fragments of the accelerators. Consequently, there has been an interest in replacing these accelerators with primary amine-based or dibenzylamine-based products which have less tendency to form toxic nitrosamines.[26]

A new Goodrich accelerator has a secondary amine radical from morpholine but situated on a thiocarbamyl group from which it does not readily release the amine.[27]



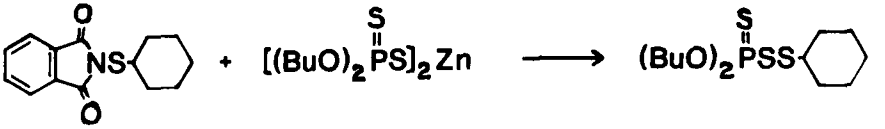
Akzo's new thiuram disulfide accelerator uses a secondary amine, dibenzylamine, but this amine has been shown not to produce a carcinogenic nitrosamine.[28,29]

A new approach to the classic problem of avoiding reversion (crosslink degradation) without loss of stress resistance is Monsanto's development of a bifunctional Bunte salt.[30]

$$NaOSO_2S(CH_2)_6SSO_2ONa$$

The inclusion of this salt in vulcanization produces thermally stable but flexible $-S_x(CH_2)_6S_x-$ crosslinks.

Monsanto has found[31,32,33] that the O,O'-dialkyl dithiophosphate accelerators, which give excellent reversion resistance, can be combined with a vulcanization retarder such as N-cyclohexylthiophthalimide to yield an unsymmetrical disulfide which has both good features - reversion resistant cure with freedom from "scorch" (premature vulcanization).



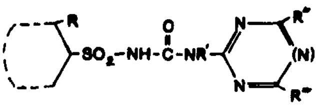
Akzo's laboratory in Obernburg, Germany has developed a catalytic air oxidation route to thiuram disulfides[34] and a similar process for sulfenamides.[35] The importance of such routes is that they have an environmental advantage, avoiding the formation of byproducts. Akzo has also recently announced manufacture of mercaptobenzothiazole by a new process (not disclosed) which avoids troublesome byproducts.[35a]

New sulfur-containing antioxidants for rubber continue to be discovered. A dodecylthiomethylated polyphenol recently made at Goodyear[36,37] has been found to be a self-synergizing antioxidant for uncured rubber.

SULFUR-BASED AGRICULTURAL CHEMICALS

Sulfur continues to be important in agrochemicals, as shown by the large variety of new sulfur-based crop-protection chemicals in current development around the world.[38,38a,b] The scope of the present review allows for discussion of only a few selected examples.

The sulfonylurea herbicides[39] are about one to two orders of magnitude more active than the classical herbicides used for weed control in agriculture. These sulfonylureas all share a common structural pattern.



The variations in the "right side" of the molecule as depicted above are relatively few; triazine and pyrimidine rings are allowed and substituents can be methyl, methoxy, or other small radicals. On the "left side", many variations are possible with a wide variety of aromatic, heterocyclic, and even aliphatic groups, nevertheless with very precise steric and electronic demands. Selectivity against various plant species is controlled by these structural variations.

The sulfonylureas have been shown to be powerful inhibitors of acetolactic synthase, a key enzyme present in plants which is essential for the synthesis of branched chain amino acids, valine, leucine and isoleucine. The exact molecular site of action seems not to have been established as yet, although considerable information about it is known.[40,41] The binding site of the herbicide is close to but not exactly at the binding site for the natural pyruvate substrate.

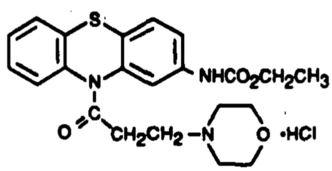
The manufacture of the sulfonylureas is described in the patent literature by way of the sulfonylisocyanates, which in turn are made from the sulfonamides by reaction with butyl isocyanate.[42]

A potentially large volume product, in terms of the amount of sulfur which might be consumed, is sodium tetrathiocarbonate, a new soil fumigant under field development by Union Oil Co. of California.[43] This product is made from CS_2, sulfur and caustic soda. Tetrathiocarbonate gives broad spectrum control of nematodes, nitrifying bacteria, grape phylloxera and a wide range of soil fungi.[44,45] It is water soluble and can be added with irrigation water. Being low in phytotoxicity, it can be used even on some established plants such as citrus trees and grape vines.

Familiar sulfur-containing agrochemical types continue to have new variations, mostly in the direction of increased activity on the target organisms and improved selectivity towards crops and other non-target organisms. Thus, new S-benzylthiolcarbamate herbicides and new S-alkylthiophosphate anticholinesterase insecticides have recently been introduced.[38]

In the manufacture of agricultural chemicals, several new technologies have been developed for some of the key intermediates. One area of current activity is the use of air oxidation in place of chemical reagents where an oxidative step is required. In the laboratory at Stauffer Chemical Co. (which is now part of Akzo Chemical Co.), an air oxidation process was developed for converting methyl dithiocarbamate to methyl isothiocyanate, carried out with a metal catalyst in the presence of a quaternary ammonium compound.[46]

Touching briefly on pharmaceuticals, a new phenothiazine-based drug, moricizine,

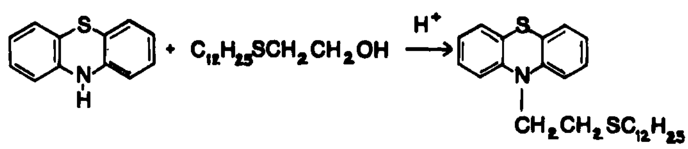


effective against heart ventricular arrhythmias, was developed in the Academy of Medical Sciences in Moscow, and licensed recently to DuPont Pharmaceuticals for commercial introduction as Ethmozine.[47]

OIL ADDITIVES

The traditional sulfurized olefins, used for many decades, continue to have an important place in extreme pressure lubrication. There is some tendency now to avoid using halogen-containing components. In this connection, it has been recently found that the adducts of sulfur chloride and olefins can be dehydrochlorinated surprisingly well by just warming in the presence of a polar solvent such as formic acid.[48] There is also a trend towards getting rid of the metal content of oil additives - to change over to the so-called ashless types. It is hard to ascertain which additives are of this type are actually in commercial use, but to illustrate, a recent Exxon patent shows the use of a combination of an ashless dispersant, a sulfurized alkylphenol and a polysulfide derivative of 2,5-dimercaptothiadiazole as a heavy-duty lubrication oil additive system.[49] Mobil recently disclosed a new type of metal-free halogen-free oil additive, a sulfinylbis(dithiophosphate).[50]

Along with load-bearing oil additives, oil-soluble antioxidants are important to protect oil from deterioration. Lubrizol found that by replacing the labile hydrogen on the phenothiazine nitrogen by an alkylthioethyl group, using alkylthioethanol as alkylating agent, the stabilizing activity was surprisingly increased.[51]



SULFUR-BASED SURFACTANTS

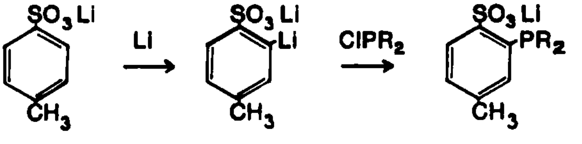
The linear alkylbenzenesulfonates continue to be the largest volume synthetic surfactants;[52] here, progress is not in the basic chemistry but in the engineering of the sulfonation process.[53] However, Stepan has recently developed a series of alpha-sulfonated fatty esters, made by direct reaction of the ester with SO_3.[54] These products are mild to the skin, and are good hydrotropic ingredients and lime soap dispersants. Being made from a vegetable oil source, they are not dependent on petrochemicals.

A new series of nonionic sulfur-based metal cleaning surfactants is under development by Phillips Petroleum Co. These are made by partially oxidizing an alkylpoly-oxyethylenethioalkanol to the sulfoxide.[55]

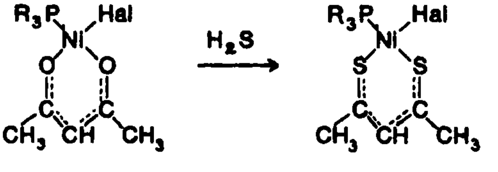
SULFUR-BASED LIGANDS IN CATALYSIS

The use of sulfonic acid groups in phosphine ligands has attained some importance. A well-established example is the sulfonated triphenylphosphine used in Rhone-Poulenc's proprietary hydroformylation process. The water-soluble ligand makes product separation and catalyst recovery easier.

Recently, work at Union Carbide Corp. has shown that a triphenylphosphine with an ortho-sulfo group is an especially useful bidentate ligand which, when bound to nickel, produces an active and highly selective catalyst for production of even-numbered alpha-olefins from ethylene.[56]



Research in Australia has uncovered a superactive, almost enzyme-like, catalyst for olefin oligomerization, although not highly selective. This is a readily-made complex of nickel with dithioacetylacetone and a phosphine.[57]



SULFUR DYES

The largest volume dyes are still the sulfur dyes. The largest volume sulfur dye is still C. I. Sulfur Black 1 (C. I. 53185).[58] It is interesting that the chemical structure of Sulfur Black 1 is still not known![59]

New developments in sulfur dye technology have been stimulated by the problems of waste disposal. Up till recently, the reduction of sulfur dyes to the leuco form has often been performed using sulfide, which has obvious pollution problems. Recently, it has been shown that this reduction can be carried out by a reducing sugar, so that the byproducts and any unused reducing agent are readily biodegradable to harmless products.[60]

SULFUR-BASED TEXTILE FINISH

A successful commercial development of recent years is the stain-resistant carpet. The technology is based on certain sulfonated phenolic resins based on 4,4'-sulfonylbisphenol) which are substantive to the carpet fiber, generally nylon.[61]

SULFUR-BASED PERSONAL CARE PRODUCTS

The use of thioglycolic acid salts in hair waving preparations is well established but innovations continue to be made. Sulfite for "softer" curling is a more recent development, but the reduction of the hair disulfide linkages by sulfite is slow. A recent disclosure shows that a microbiologically-derived sulfur compound, thioredoxin, or a thioredoxin-like dithiol peptide, can catalyze the reduction of hair disulfide links by sulfite.[62]

OUTLOOK AND GENERAL COMMENTS

The chemical versatility and low cost of sulfur make it a very attractive element for industrial products. However, we can expect environmental pressures regarding sulfur-containing byproducts. Therefore, it is advisable that in any research and development program in applied sulfur chemistry, attention should be directed to avoidance of troublesome byproducts. This requirement also presents an excellent stimulus for the invention of new sulfur chemistry.

REFERENCES

1. A. Duda and S. Penczek, in Encyclopedia of Polymer Science and Engineering, H. Mark et al., Eds., 2nd Edition, Vol. 16, John Wiley & Sons, New York, 1989, pp. 246-368.
2. L. C. Lopez and G. L. Wilkes, J. Macromol. Sci. - Rev. Macromol. Chem. Phys. C29 (1), 83-151 (1989).
3. J. Geibel and R. W. Campbell, in Comprehensive Polymer Science, Vol. 5, Step Polymerization, G. C. Eastmond et al., Eds., Pergamon Press, Oxford, 1989, Ch. 32, pp. 543-560.
4. K. Kohlhepp, Kunststoffe 79 (7), 602-5 (1989).
5. D. M. Lee and R. W. Campbell, Polymer News 14, 73-81 (1989).
6. R. H. Massey, in Conference Proceedings, SPE ANTEC, May 7-11, 1990, pp. 1648-1651.
7. C.-C. M. Ma, L.-T. Hsiue, W.-G. Wu, and W.-L. Liu, J. Appl. Polym. Sci. 39, 1399-1415 (1990).
8. Y. Iizuka, T. Iwasaki, T. Katto and Z. Shiiki (to Kureha Kagaku Kogyo KK), U. S. Pat. 4,645,826 (1987).

8a. K. Idol, D. Freitag and L. Bottenbruch (to Bayer), U. S. Pat. 4,433,138 (1984); E. Ostlinning and K. Idol (to Bayer), U. S. Pat. 4,663,430 (1987).

8b. M. Rule, D. R. Fagerburg, J. J. Watkins and J. S. Fauver (to Eastman Kodak), U. S. Pats. 4,786,713, 4,792,600 (1988), 4,855,393, 4,857,629 and 4,859,762 (1989).

9. E. Tsuchida, K. Yamamoto, M. Jikei and H. Nishide, Macromol. 22, 4138-40 (1989);ibid. 23, 2101-6 (1990).

10a. J. F. Geibel, R. G. Gaughan and M. D. Cliffton (to Phillips Petroleum), U. S. Pat. 4,892,929 (1990); M. D. Cliffton and J. F. Geibel (to Phillips Petroleum), U. S. Pat. 4,812,552 (1989).

10b. Y. Satake, T. Kaneko, Y. Kobayashi, Y. Iizuka, T. Katto and Z. Shiiki (to Kureha), U. S. Pat. 4,886,871

(1989).
10c.S. Tomagou, T. Kato and K. Ogawara (to Tosoh Corp.), Eur. Pat. Appl. 346,085 (publ. Dec. 13, 1989).
10d.Anon., High Perform. Plast. 6 (3), 4-5 (1989).
11. R. A. Clendinning, A. G. Farnham and R. N. Johnson, in High Performance Polymers; Their Origin and Development, R. B. Seymour and G. S. Kirshenbaum, Eds., Elsevier Science Publ. Co., New York, 1986, pp. 149-157.
11a.R. W. Campbell (to Phillips Petroleum), U. S. Pat. 4,016,145 (1977).
12. G. T. Kwiatkowski, M. E. Sauers and M. Matzner, in High Temperature Polymers and Their Uses, Symposium of SPE, Special Int. Group, Cleveland Section and Center of Appl. Polym. Res., Case Western Reserve Univ., Oct. 2-4, 1989, pp. 47-63.
13. M. S. Reisch, C&EN Sept. 4, 1989, 21-49.
14. P. A. Staniland, Bull. Soc. Chim. Belg. 98 (9-10), 667-676 (1989).
14a.N. Tamai, K. Kashiwame, and S. Ozawa (to Asahi Glass Co.), Jpn. Kokai Tokkyo Koho 63,256,653 (Oct. 24, 1988).
15. I. Colon and G. T. Kwiatkowski, J. Polym. Sci.: Part A: Polym. Chem. 28, 367-383 (1990).
16. R. L. Elsenbaumer, K. Y. Jen, G. G. Miller, and L. W. Shacklette, Synthetic Metals 18, 277-282 (1987).
17. J. Osterholm, J. Laakso, P. Nyholm, H. Isotalo, H. Stubb, O. Inganas, and W. R. Salaneck, Synthetic Metals 28, C435-C444 (1989); J. Laakso, J. Osterholm and P. Nyholm, Synthetic Metals 28, C467-471 (1989).
18. Y. Ikenoue, N. Uotani, A. O. Patil, F. Wudl, and A. J. Heeger, Synthetic Metals 30 (3), 305-319 (1989).
19. C. C. Han and R. L. Elsenbaumer, Synthetic Metals 30, 123-131 (1989).
20. S. A. Jenekhe, Macromol., in press (1990).
21. S. A. Jenekhe, S. K. Lo, and S. R. Flom, Appl. Phys. Lett. 54 (25), 2524-6 (1989).
22. W. C. McBee, H. H. Weber, and W. T. Dohner, Structural Materials Proceedings, Structures Congress '89, ASCE, San Francisco, CA, May 1-5, 1989, 31-43.
23. R. J. Timmons, Paper presented at Div. Fertilizer & Soil Chem., ACS National Meeting, Sept. 10-15, 1989; W. C. McBee, H. H. Weber and E. A. Krabbe, ibid.; papers available from the Sulfur Institute, Washington, DC.
23a.B. Bordoloi, E. M. Pearce, L. Blight, B. R. Currell, R. Merrall, R. A. M. Scott and C. Stillo, J. Polym. Sci., Polym. Chem. Ed. 18 (2), 383-406 (1980).
23b.P. Kalb and P. Columbo, Report BNL 51923, "Modified Sulfur Cement Solidification of Low-Level Wastes," Brookhaven National Laboratory, Oct. 1985.
23c.P. D. Kalb, J. H. Heiser and P. Columbo, paper no. BNL-43691, in Proceedings of the Incineration Conference, San Diego, CA, May 14-18, 1990.

23d. A. Van Dalen and J. E. Rijpkema, paper IAEA-SM-303/3P in Proceedings of International Symposium on Management of Low and Intermediate Level Radioactive Wastes, Stockholm, May 16-20, 1988, published by IAEA, Vienna, 1989.
24. Anon., C&EN, Oct. 2, 1989, 26.
25. R. D. Lundberg, R. R. Phillips, and D. G. Peiffer, J. Polym. Sci.: Part B: Polym. Phys. 27, 245-260 (1989).
25a. W. E. Walles, D. R. Near and D. L. Tomkinson (to Dow Chemical Co.), U. S. Pat. 4,902,493 (1990); W. E. Walles and D. L. Tomkinson (to Dow Chemical Co.), U. S. Pat. 4,915,912 (1990); anon., Plast. Eng., Aug. 1990, 14-5.
26. K. M. Davies, D. G. Lloyd and A. Orband, Kautsch. Gummi Kunstst. 42 (2), 120-3 (1989).
27. D. W. Chasar, Kautsch. Gummi. Kunstst. 42 (1), 31-3 (1989).
28. D. Seeburger, paper at Rubber Conference, Tampere, Finland, Jan. 1989.
29. G. Raabe, D. Seeberger and P. Boite, Kautsch. Gummi Kunstst. 41 (11), 1097-8 (1988).
30. A. Anthoine, E. R. Lynch and A. F. Devaux, paper at meeting of Rubber Div., ACS, Las Vegas, Nev., May 29-Jun. 1, 1990.
31. K. Morita, A. B. Sullivan and A. Y. Coran, Rubber Chem. Tech. 58 (2), 284-294 (1985).
32. L. H. Davis, A. B. Sullivan and A. Y. Coran, Rubber Chem. Tech. 60, 126-139 (1987).
33. B. H. To, L. H. Davis, R. W. Faulkner and W. W. Paris, Plast. Rubber Processing and Applications 12 (2), 89-104 (1989).
34. H. Zengel, L. Eisenhuth, and M. Bergfeld (to Akzo NV), U. S. Pat. 4,670,556 (1987).
35. M Bergfeld, H. Zengel and H. Praetorius (to Akzona, Inc.), U. S. Pat. 4,316,031 (1982).
35a. S. Stinson, C&EN, May 21, 1990, 45-66.
36. B. H. Sturm and J. A. Kuczkowski (to Goodyear Tire & Rubber Co.), U. S. Pat. 4,707,300 (1987).
37. J. A. Kuczkowski, B. H. Sturm, K. S. Cottman, D. C. Grimm and J. J. Dillon, paper given at 134th Meeting of the Rubber Div., ACS, Cincinnati, Ohio, Oct. 18-21, 1988.
38. W. L. Hopkins, Ag Chem New Product Review, Vol. 8, William L. Hopkins Ag Chem. Information Services, Indianapolis, IN, 1990.
38a. T. G. Cullen, A. J. Martinez, J. M. Willut, and C. P. DiSanzo, and J. J. Vukich, Abstr. Div. Agrochem., ACS 199th National Meeting, Boston, Apr. 22-27, 1990, papers 10-12.
38b. R. E. Hackler, T. W. Waldrep, S. V. Kaster, K. W. Burow and D. I. Wickiser, Abstr. Div. Agrochem., ACS 199th National Meeting, Boston, Apr. 22-27, 1990, paper 31.
39. J. V. Schloss, Accounts of Chem. Res. 21, 348-373

(1988).
40. J. V. Schloss and A. Aulabaugh, in Biosynthesis of Branched Chain Aminoacids, Z. Barak, D. M. Shipman and J. V. Schloss, Eds., VCH, Weinheim, 1990, 329-356.
41. J. V. Schloss, in P. Boger and G. Sandmann, Eds., Target Sites of Herbicide Action, CRC Press, Boca Raton, FL, 1989, 165-245, see also pp. 114-125.
42. J. J. Reap (to E. I. Du Pont de Nemours & Co.), U. S. Pat. 4,629,496 (1986) and many related patents to this assignee.
43. D. C. Young and J. A. Green (to Union Oil Co. of Calif.), U. S. Pat. 4,476,113 (1984), 4,726,144 (1988).
44. M. E. Matheron and J. C. Matejka, Phytopath. 78 (9), 1234-7 (1988).
45. anon., Agrichem. Age, 33 (8), 20 (1989).
46. J. Telschow and D. A. Bright (to Stauffer Chemical Co.), U. S. Pat. 4,713,467 (1987).
47. anon., C&EN, July 2, 1990, 5-6.
48. R. L. Sowerby and S. A. DiBiase (to Lubrizol Corp.), U. S. Pat. 4,764,297 (1988).
49. G. P. Fetterman and A. A. Schetelich (to Exxon), Eur. Pat. Appl. 311318 (Apr. 12, 1989); Chem. Abs. 111:60845z.
50. A. O. Okorodudu (to Mobil Oil Corp.), U. S. Pat. 4,826,629 (1989).
51. M. F. Salomon (to Lubrizol Corp.), U. S. Pat. 4,785,095 (1986).
52. C. A. Schirber, Soap/Cosmetics/Chemical Specialties, April 1989, 32-36.
53. S. Wilk and K. Linkiewicz, Przemysl Chemiczny 64 (1), 25-28 (1985).
54. N. R. Smith, Soap/Cosmetics/Chemical Specialties, April 1989, 48-57, 130-136.
55. R. L. Bobsein and C. R. Bresson (to Phillips Petroleum Co.), U. S. Pat. 4,663,082 (1987).
56. R. E. Murray, Preprints Div. Petrol. Chem., 34 (3), ACS National Meeting, Sept. 10-15, 1989, 599-601.
57. S. J. Brown, L. M. Clutterbuck, A. F. Masters, J. I. Sachinidis and P. A. Tregloan, Appl. Catal. 48 (1), 1-11 (1989).
58. M. Dixon, Amer. Dyestuff Reporter, May 1988, 52-55.
59. R. A. Guest and W. E. Wood, Rev. Prog. Coloration 19, 63-71 (1989).
60. M. S. Carlough and L. A. Meszaros (to Sandoz Ltd.), U. S. Pat. 4,801,303 (1989); L. A. Meszaros (to Sandoz Ltd.), U. S. Pat. 4,917,706 (1990).
61. P. Harris and D. A. Hangey, Textile Chem. & Colorist, Nov. 1989, 25-30.
62. V. P. Pigiet (to Repligen Corp.), U. S. Pat. 4,894,223 (1990).