

(12) PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 199661944 B2**
(10) Patent No. **721723**

(54) Title
Polyurea-thickened grease composition

(51)⁶ International Patent Classification(s)
C10M 169/06 C10M 115/08

(21) Application No: **199661944** (22) Application Date: **1996 .08 .07**

(30) Priority Data

(31) Number	(32) Date	(33) Country
08/518775	1995 .08 .24	US
08/653549	1996 .05 .24	US

(43) Publication Date : **1997 .02 .27**

(43) Publication Journal Date : **1997 .02 .27**

(44) Accepted Journal Date : **2000 .07 .13**

(71) Applicant(s)
The Lubrizol Corporation

(72) Inventor(s)
Patricia Rachelle Todd

(74) Agent/Attorney
CALLINAN LAWRIE,Private Bag 7,KEW VIC 3101

(56) Related Art
EP 508115
US 5207935
US 3660288

ABSTRACT OF THE INVENTION

A grease composition comprising: a major amount of an oil of lubricating viscosity; a thickener selected from the group consisting of monoureas, diureas, triureas and polyureas, or mixtures thereof; and an oil soluble neutral or overbased zinc salt of a carboxylic acid selected from the group consisting of zinc salts of fatty acids, the zinc salts of hydrocarbyl-substituted salicylic acids, and zinc glyoxylates is disclosed.

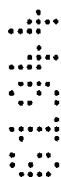
10

c:\winword\jhe\dockets\2698cip.doc

COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL



TO BE COMPLETED BY APPLICANT

Name of Applicant: THE LUBRIZOL CORPORATION



Actual Inventor: Patricia Rachelle Todd



Address for Service: CALLINAN LAWRIE, 278 High Street, Kew,
Victoria 3101, Australia



Invention Title: "POLYUREA-THICKENED GREASE COMPOSITION"

The following statement is a full description of this invention, including the best method of performing it known to us:-

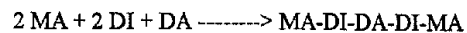
2698R-01

TITLE: POLYUREA-THICKENED GREASE COMPOSITION

This invention relates to a urea-thickened grease composition. More particularly, it relates to a urea-thickened grease composition containing oil-soluble zinc carboxylates.

BACKGROUND OF THE INVENTION

Grease compositions have been known for a long time. Classically, greases have contained an oil of lubricating viscosity and a thickening agent. Thickening agents have often been soaps, such as the metallic salts of fatty acids. Calcium soaps, as grease-thickening agents, have a long history. More recently, complex greases have been developed which use a combination of a salt of a long chain acid, such as stearic acid, and a salt of a short chain acid, such as acetic acid to form a thickening metallic salt soap. Calcium is typical metallic counter ion for this type of grease. Sodium, lithium, and aluminum have been used to form soaps which act as grease thickeners. Organophilic bentonite clays have been used as grease thickeners. More recently, ureas have been used as grease thickeners. The ureas are prepared by reacting an isocyanate with an amine. Monoureas may be prepared by reacting a monoisocyanate with a monoamine. Polyureas are prepared by reacting combinations of diamines, monoamines, diisocyanates, and monoisocyanates. A common reaction mixture includes a diisocyanate, a diamine and a monoamine. The monoamine is included in the reaction mixture since it acts to terminate the polymer chain and prevents it from becoming too long. The basic reaction is illustrated by the following equation:



Tetraurea

MA = Monoamine

DI = Diisocyanate

DA = Diamine

Additives are frequently added to grease to improve various performance properties. Among the properties which may be improved through the use of additives are oxidation stability, water resistance, rust protection, corrosion

protection, antiwear, extreme pressure, adhesiveness, color, oil separation, low temperature flow, and high temperature performance. Salicylates have been used in grease compositions, some times as part of a complex grease, and some times as additives.

5 Chinese Patents 1052890 and 1052891, as abstracted in the Derwent Database under the numbers WPI ACC NO 92-124047/16 and 92-124048/16, disclose lubricating greases containing a thickening agent which includes lithium 12-hydroxy-stearate and lithium salicylate. The salicylate appears to be an unsubstituted salicylate and is said to be part of the thickening agent.

10 U.S. Patent 3,660,288 discloses a polyurea grease containing the magnesium salts of unsaturated fatty acids. The alkali metal, other alkaline earth metal and zinc salts of ricinoleic acid were tested in the composition, but did not impart the desired rust resistance.

15 U.S. Patent 3,711,407 discloses a grease composition containing an alkali metal salt of hydroxybenzoic acid. The salt is oil insoluble and forms in small particles evenly distributed throughout the composition.

U.S. Patent 3,846,314 discloses a polyurea grease composition containing an alkaline earth aliphatic carboxylate, especially calcium acetate.

20 U.S. Patent 3,846,315 discloses polyurea greases containing alkaline earth metal 1-3 carbon monocarboxylates.

U.S. Patent 3,868,329 discloses a polyurea grease composition containing an alkaline earth metal aliphatic monocarboxylate containing from 1 to 3 carbon atoms. Calcium acetate is preferred. The composition also includes a Mannich base.

25 U.S. Patent 3,983,041 discloses a polyurea grease which contains an alkaline earth carbonate or an alkaline earth lower carboxylate. The alkaline earth salts serve as rust inhibitors.

U.S. Patent 5,246,605 discloses a polyurea grease containing antimony dipentylthiocarbamate. The antimony salt provides extreme pressure and antiwear properties to the grease.

U.S. Patent 4,719,023 discloses a grease composition which comprises a base fluid, a thickener, a calcium salicylate and a magnesium salicylate. The salicylates may be neutral but are preferably overbased alkyl salicylates. The calcium salicylate improves anti-rust properties, and the magnesium salicylate counteracts the decrease in dropping point caused by the addition of the calcium salicylate. The thickener may be a substituted urea; however, the preferred thickening agent is an alkali fatty acid soap.

U.S. Patent 4,828,733 discloses greases containing the cuprous salt of 4-hydroxybenzoic acid (salicylic acid is 2-hydroxybenzoic acid). The salts are primarily antioxidants. However, friction-reducing and wear protection are also disclosed.

U.S. Patent 4,929,369 discloses a grease which may be thickened with polyurea and which includes a monovalent salt of a carboxylic acid in which the -COOH group is attached to a ring atom of a fused ring system.

U.S. Patent 5,011,617 discloses a polyurea-thickened grease and an alkaline earth salt of a 1-3 carbon aliphatic monocarboxylate.

U.S. Patent 5,084,193 discloses a polyurea grease which contains in addition a simple or complex calcium soap as a further thickener.

U.S. Patent 5,207,935 discloses a polyurea grease containing a calcium, barium, magnesium or zinc salt of an alkylsuccinic acid, such as dodecenylsuccinic acid in combination with a sulfonate. The succinic salt acts as a rust inhibitor and texture improver.

Japanese Patent 3035091 discloses greases thickened with lithium and sodium soaps which include a wide variety of anti-static agents including magnesium oleate, copper oleate and chromium alkylsalicylate.

Japanese Patent 57212297 discloses a lithium grease which includes alkaline earth salicylates.

British Patent 2,215,346 discloses grease compositions thickened with lithium soap, lithium borate, lithium hydroxy-benzoate and a polyol. The lithium hydroxy-

benzoate is either the lithium salt of a hydroxy-benzoic acid or the lithium salt of a low alcohol ester of such an acid.

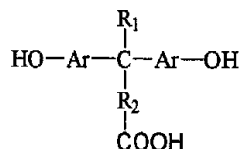
EP Patent 84,910 discloses a lithium complex grease composition which includes lithium salicylate as a complexing agent.

5 EP Patent 151,825 discloses a continuous process for manufacturing lubricating greases in which the thickener is a soap and various complexing agents, such as acetic and salicylic acid, may be added.

EP Patent 566,326 discloses a polyurea grease with molybdenum dialkyldithiophosphates and ashless dithiophosphates as additives.

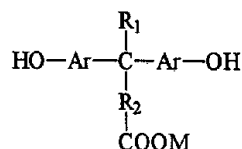
10 Soviet Patent SU 924089 discloses a grease containing a high ash calcium alkylsalicylate. The calcium alkylsalicylate prevents stratification.

U.S. Patent 2,933,520 to Bader relates to compounds represented by the formula:



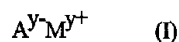
in which R₁ may be hydrocarbon, halogen, such a chlorine or the like, and R₂ is
15 hydrocarbon, e.g., alkylene, other than methylene, containing at least two carbon atoms such as ethyl, propyl, butyl, with either normal, or branched chains and containing, for example, up to 10, 12 or even more carbon atoms. The Ar groups are aromatic rings. They may be unsubstituted, but one or both thereof can contain substituents such as alkyl (methyl, ethyl, propyl, butyl, isopropyl, isobutyl), halogen, (chlorine, bromine), nitro, sulfo
20 and others. The nature of each of these groups affecting properties such as boiling point, solubility, toxicity, and bactericidal, fungicidal, insecticidal and like properties.

U.S. Patent 3,133,944 to Christensen teaches heavy metal salts represented by:

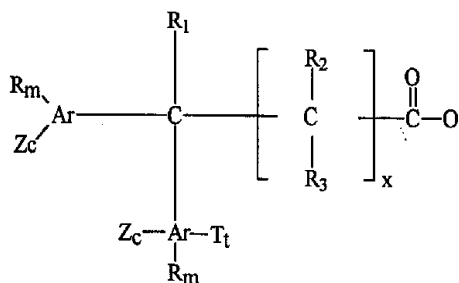


wherein the R_1 is an alkyl of 1-4 carbons, R_2 is an alkylene of 2-6 carbons and Ar is an aromatic group which may be substituted with one or more methyl groups and others. The salts are said to be adapted to retard or prevent the growth of biological organisms, particularly molds and mildews.

U.S. Patent 5,356,546 relates to metal salts of the general formula:



wherein M represents one or more metal ions, y is the total valence of all M, and A represents one or more anion containing groups having a total of about y individual anionic moieties and each anion containing group is a group of the formula:



wherein T is an organic group selected from a group of structures, t is 0 or 1, R is an alkyl, alkenyl or aryl group containing at least 8 carbon atoms, R_1 , R_2 , and R_3 are independently H or a hydrocarbyl group, m is an integer from 1 to 10, c is an integer such that the sum of m, c and t does not exceed the valence capacity of Ar, and Z is OH, OR_4 or O^- . The salts find utility in lubricants and fuels compositions.

Summary of the Invention

According to the present invention there is provided a grease composition comprising a major amount of an oil of lubricating viscosity and an additive further comprising (A) a thickener selected from the group of mono-ureas, di-ureas, tri-ureas and polyureas and mixtures thereof, and (B) an oil-soluble neutral or overbased zinc salt of a carboxylic acid selected from the group consisting of zinc salts of fatty acids, the zinc salts of hydrocarbyl-substituted salicylic acids and zinc glyoxylates, provided that if (B) is the zinc salt of a fatty acid, the fatty acid is not ricinoleic acid.

According to a further embodiment of the present invention there is provided a method of lubricating metal surfaces which move with respect to each other which comprises placing between said metal surfaces an appropriate quantity of a grease composition comprising (of) a major amount of an oil of lubricating viscosity, a thickener selected from the group consisting of mono-ureas, di-ureas, tri-ureas and polyureas and mixtures thereof, and an oil-soluble neutral or overbased zinc salt of a carboxylic acid selected from the group consisting of zinc salts of fatty acids, the zinc salts of hydrocarbyl-substituted salicylic acids, and zinc glyoxylates, provided that if the zinc salt is a zinc salt of a fatty acid, the fatty acid is not ricinoleic acid.

Detailed Description of the Invention

Surprisingly, it has been found that the oil-soluble zinc carboxylates act as antiwear additives in urea-thickened greases. The preferred oil-soluble zinc carboxylates are the salts of fatty acids, the salts of hydrocarbyl-substituted salicylic acids, and the salts of the reaction product of glyoxylic acid and hydrocarbyl substituted phenols, herein referred to as zinc glyoxylates. The term zinc glyoxylates is used to describe the zinc salts of the bis (hydrocarbyl substituted hydroxyaryl) acetic acids produced in the reaction between the glyoxylic acid and a phenol.

As will be set forth more fully below, the zinc carboxylates are neutral, to moderately overbased, and the urea greases may be thickened monourea, diurea, triurea, or polyurea thickeners. Moderately over based means a conversion of between 100 and 200.



The term "hydrocarbyl" is used herein to include:

- (1) hydrocarbyl groups, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic groups and the like as well as cyclic groups wherein the ring is completed
5 through another portion of the molecule (that is, any two indicated groups may together form an alicyclic group);
- (2) substituted hydrocarbyl groups, that is, those groups containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl nature of the hydrocarbyl group; those skilled in the art
10 will be

3
5
6
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
219

aware of such groups, examples of which include ether, oxo, halo (e.g., chloro and fluoro), alkoxy, mercapto, alkylmercapto, nitro, nitroso, sulfoxy, etc.;

(3) hetero groups, that is, groups which, while having predominantly hydrocarbyl character within the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be
5 apparent to those of skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as pyridyl, furanyl, thiophenyl, imidazolyl, etc.

In general, no more than about three nonhydrocarbon groups or heteroatoms, and preferably no more than one, will be present for each ten carbon atoms in a
10 hydrocarbyl group. Typically, there will be no such groups or heteroatoms in a hydrocarbyl group and it will, therefore, be purely hydrocarbyl.

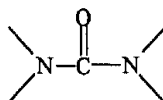
The hydrocarbyl groups are preferably free from acetylenic unsaturation; ethylenic unsaturation, when present, will generally be such that there is no more than one ethylenic linkage present for every ten carbon-to-carbon bonds. The hydrocarbyl
15 groups are often completely saturated and therefore contain no ethylenic unsaturation.

Overbased salts of organic acids are widely known to those of skill in the art and generally include metal salts wherein the amount of metal present in them exceeds the stoichiometric amount. Such salts are said to have conversion levels in excess of 100 (i.e.,
20 they comprise more than 100% of the theoretical amount of metal needed to convert the acid to its "normal" or "neutral" salt). Such salts are often said to have metal ratios in excess of one (i.e., the ratio of equivalents of metal to equivalents of organic acid present in the salt is greater than that required to provide the normal or neutral salt which required only a stoichiometric ratio of 1:1). They are commonly referred to as overbased, hyperbased or superbased salts. The zinc salts useful in the present invention are
25 moderately overbased, that is, they have a conversion between 100 and 200.

The terminology "metal ratio" is used in the prior art and herein to designate the ratio of the total chemical equivalents of the metal in the overbased salt to the chemical equivalents of the metal in the salt which would be expected to result in the reaction between the organic acid to be overbased and the basically-reacting metal compound according to the known chemical reactivity and stoichiometry of the two reactants. Thus, in a normal or neutral salt the metal ratio is one, and in an overbased salt the metal ratio is greater than one.

A. UREA GREASE THICKENERS

The greases used in the present invention are thickened with various substituted ureas. The ureas are mono-, di-, tri- or polyureas. The mono-, di-, tri- or polyurea component of this invention is a water and oil insoluble organic compound having a molecular weight between about 375 and 3,400 and having at least one ureido group and preferably between about 2 and 8 ureido groups. A ureido group as referred to herein is defined as

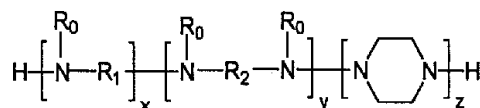


A particularly preferred polyurea compound has an average between 3 and 4 ureido groups and has a molecular weight between about 600 and 1200.

In one embodiment, the mono-, di-, tri- or polyurea compounds are prepared by reacting the following components:

I. A diisocyanate having the formula: OCN--R--NCO wherein R is a hydrocarbylene having from 2 to 30 carbons and preferably from 6 to 15 carbons and more preferably 7 carbons.

II. A polyamine having a total of 2 to 40 carbons and having the formula:



wherein

5 R_1 and R_2 are the same or different type of hydrocarbylenes having from 1 to 30 carbons and preferably from 2 to 10 carbons and more preferably from 2 to 4 carbons;

R_0 is selected from hydrogen or a $\text{C}_1\text{-C}_4$ alkyl and preferably hydrogen;

x is an integer from 0 to 4;

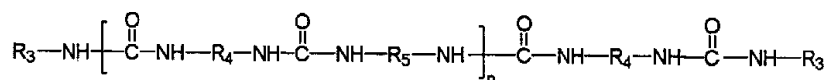
10 y is 0 or 1; and

z is an integer equal to 0 when y is 1 and equal to 1 when y is 0.

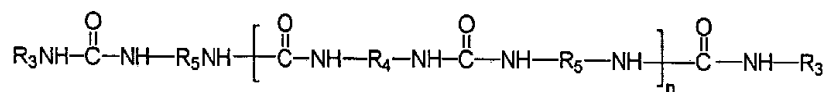
III. A monofunctional compound selected from the group consisting of
 15 monoisocyanate having 1 to 30 carbons, preferably from 10 to 24 carbons, a
 monoamine having from 1 to 30 carbons preferably from 10 to 24 carbons, and
 mixtures thereof.

The reaction can be conducted by contacting the three reactants in a suitable
 reaction vessel at a temperature between about 60 to 320°F (16 to 169°C), preferably
 from 100 to 300°F (38 to 149°C) for a period from 0.5 to 5 hours and preferably
 from 1 to 3 hours. The molar ratio of the reactants present usually varies from 0.1-2
 20 moles of monoamine or monoisocyanate and 0-2 moles of polyamine for each mole
 of diisocyanate. When the monoamine is employed, the molar quantities are
 preferably $(n + 1)$ moles of diisocyanate, (n) moles of diamine and 2 moles of
 monoamine. When the monoisocyanate is employed, the molar quantities are
 preferably (n) moles of diisocyanate, $(n + 1)$ moles of diamine and 2 moles of
 25 monoisocyanate.

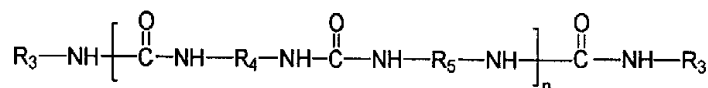
A particularly preferred class of mono-, di-, tri- or polyurea compounds has structures defined by the following general formulae:



FORMULA 1



FORMULA 2



FORMULA 3

wherein:

n is an integer from 0 to 4;

R₃ is the same or different hydrocarbyl having from 1 to 30 carbon atoms, preferably from 10 to 24 carbons;

R₄ is the same or different hydrocarbylene having from 2 to 30 carbon atoms, preferably from 6 to 15 carbons; and

R₅ is the same or different hydrocarbylene having from 1 to 30 carbon atoms, preferably from 2 to 10 carbons.

The hydrocarbylene, as defined in R₁ and R₂ above, is a divalent hydrocarbon radical which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., alkylarylene, aralkylene, alkylcycloalkylene, cycloalkylarylene, etc., having its two free valences on different carbon atoms.

The mono-, di-, tri- or polyureas having the structure presented in Formula 1 above are prepared by reacting (n + 1) moles of diisocyanate with two moles of a monoamine and (n) moles of a diamine. (When n equals zero in the above Formula 1,

the diamine is deleted.) Mono-, di-, tri- or polyureas having the structure presented in Formula 2 above are prepared by reacting (n) moles of a diisocyanate with (n + 1) moles of a diamine and two moles of a monoisocyanate. (When n equals zero in the above Formula 2, the diisocyanate is deleted.) Mono-, di-, tri- or polyureas having
5 the structure presented in Formula 3 above are prepared by reacting (n) moles of a diisocyanate with (n) moles of a diamine and one mole of a monoisocyanate and one mole of a monoamine. (When n equals zero in Formula 3, both the diisocyanate and diamine are deleted.)

In preparing the above mono-, di-, tri- or polyureas, the desired reactants
10 (diisocyanate, monoisocyanate, diamine and monoamine) are admixed within a suitable reaction vessel in the proper proportions. The reaction may proceed without the presence of a catalyst and is initiated by merely contacting the component reactants under conditions conducive for the reaction. The reaction itself is exothermic and, accordingly, by initiating the reaction at room temperature, elevated
15 temperatures are obtained. However, external heating or cooling may be desirable.

REACTANTS

The monoamine or monoisocyanate used in the formulation of the mono-, di-, tri- or polyurea will form the terminal end groups. These terminal end groups will have from 1 to 30 carbon atoms, but are preferably from 5 to 28 carbons, and more
20 desirably from 6 to 25 carbon atoms.

Illustrative of various monoamines are pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, dodecenylamine, hexadecenylamine, octadecenylamine, octadecadienylamine, abietylamine, aniline, toluidene,
25 naphthylamine, cumylamine, bornylamine, fenchylamine, tertiary butyl aniline, benzylamine, beta-phenethylamine, etc. Particularly preferred amines are prepared from natural fats and oils or fatty acids obtained therefrom. These starting materials can be reacted with ammonia to give first amides and then nitriles. The nitriles are then reduced to amines, conveniently by catalytic hydrogenation. Exemplary amines

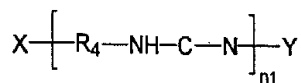
prepared by the method include stearylamine, laurylamine, palmitylamine, oleylamine, petroselinylamine, linoleylamine, linolenylamine, eleostearylamine, etc. The unsaturated amines are particularly preferred.

Illustrative of monoisocyanates are hexylisocyanate, decylisocyanate, dodecylisocyanate, tetradecylisocyanate, hexadecylisocyanate, phenylisocyanate, cyclohexylisocyanate, xyleneisocyanate, cumeneisocyanate, abietylisocyanate, cyclooctylisocyanate, etc.

The polyamines, which form the internal hydrocarbon bridges between the ureido groups usually contain from 2 to 40 carbons and preferably from 2 to 30 carbon atoms, more preferably from 2 to 20 carbon atoms. Exemplary polyamines include diamines such as ethylenediamine, propanediamine, butanediamine, hexanediamine, dodecanediamine, octanediamine, hexadecanediamine, cyclohexanediamine, cyclooctanediamine, phenylenediamine, tolylenediamine, xylenediamine, dianiline methane, ditoluidinemethane, bis(aniline), bis(toluidine), piperazine, etc., triamines, such as aminoethyl piperazine, diethylene triamine, dipropylene triamine, N-methyl-diethylene triamine, etc., and higher polyamines such as triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, etc.

Representative examples of diisocyanates include hexanediisocyanate, decanediisocyanate, octadecanediisocyanate, phenylenediisocyanate, tolylenediisocyanate, bis(diphenylisocyanate), methylene bis(phenylisocyanate), etc.

Another preferred class of mono-, di-, tri- or polyurea compounds which may be successfully employed in the practice of this invention include the following:



wherein:

n^1 is an integer of 0 to 8, R_4 is the same or different hydrocarbylene having from 2 to 30 carbon atoms, preferably from 6 to 15 carbons; X and Y are monovalent radicals selected from TABLE I below.

5

TABLE I

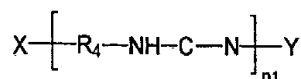
<u>X</u>	<u>Y</u>
$\text{R}_7-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{NH}-$	$\text{R}_7-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{NH}-\text{R}_5$
$\begin{array}{c} \text{O} \\ \text{ } \\ \text{R}_6-\text{C}-\text{N}- \\ \text{ } \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \text{ } \\ \text{R}_6-\text{C}-\text{N}-\text{R}_5- \\ \text{ } \\ \text{O} \end{array}$
10	R_8-

In the Table, R_5 is the same or different hydrocarbylene having from 1 to 30 carbon atoms, preferably from 2 to 10 carbons; R_8 is the same or different hydrocarbyl having from 1 to 30 carbon atoms, preferably from 10 to 24 carbons; R_6 is selected from the group consisting of arylene radicals of 6 to 16 carbon atoms and alkylene groups of 2 to 30 carbon atoms, and R_7 is selected from the group consisting of alkyl radicals having from 10 to 30 carbon atoms and aryl radicals having from 6 to 16 carbon atoms.

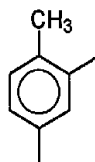
15

20

Tolylene polyurea-thickened greases, wherein at least one R₄, in the following formula, is tolylene are well known.



By tolylene it is meant a divalent organic radical having its two free valences on different carbon atoms of a methylbenzene moiety. For example, "2,4-tolylene" refers to:



The mono-, di-, tri- or polyurea compounds are prepared by blending the several reactants together in a suitable reaction vessel and heating them to a temperature ranging from 70°F to 400°F for a period sufficient to cause formation of the compound, generally from 5 minutes to 1 hour. The reactants can be added all at once or sequentially.

Examples of suitable diisocyanates, monoisocyanates, monoamines and polyamines are described supra.

The mono-, di-, tri- or polyurea compounds are generally mixtures of compounds having structures wherein n¹ varies from 0 to 4, or n¹ varies from 1 to 3, existent within the grease composition at the same time. For example, when a monoamine, a diisocyanate and a diamine are concurrently present within the reaction zone, as in the preparation of mono-, di-, tri- or polyureas having the structure shown in Formula 2, some of the monoamine may react with both sides of the diisocyanate to form a diurea. In addition to the formulation of diurea, simultaneous reactions can be occurring to form the tri-, tetra-, penta-, hexa-, octa-, etc., ureas. Particularly good results have been realized when the polyurea compound has an average of four ureido groups.

The amount of mono-, di-, tri- or polyurea compound in the final grease composition will be sufficient to thicken the base oil to the consistency of grease when combined with the alkaline earth metal carboxylate. Generally, the amount of mono-, di-, tri- or polyurea will range from 1 to 15 weight percent and preferably from 2 to 7 weight percent of the final grease composition.

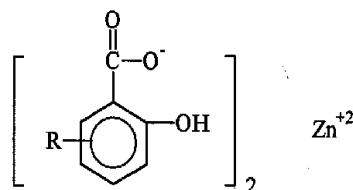
The polyureas of the above formula are readily prepared by mixing diamines and diisocyanates with monoisocyanates or monoamines in the proper proportions to form the desired polyurea. The greases thickened with the polyureas are useful at temperatures from about 100°F to 500°F. They are stable and remain oily after long use, not becoming hard or brittle. The grease compositions thus formed are extremely resistant to emulsification in water.

B. ANTIWEAR ADDITIVES

As set forth below, the antiwear additives of the present invention are oil soluble, neutral or overbased zinc carboxylates.

Zinc Hydrocarbyl salicylate

The zinc hydrocarbyl salicylate may be symbolized by the following formula:



wherein R is a hydrocarbyl group containing from about 7 to about 40 carbon atoms. The R group may be any hydrocarbyl group; however, alkyl groups containing from 7 to 40 carbon atoms are preferred. Alkyl groups containing about 7 to about 24 carbon atoms are more preferred, and alkyl groups containing about 12 to about 18 carbon atoms are most preferred. The zinc salts may be neutral, and may be prepared from neutral sodium hydrocarbyl salicylates by metal exchange. In this method of

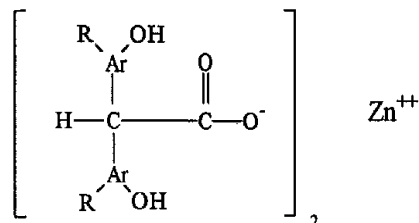
preparation, the sodium salicylate is treated with a zinc salt, such as zinc chloride, to give the desired zinc salt. In another method of preparation, an alkali metal phenate along with an excess of an alkali metal hydroxide is treated with carbon dioxide. The product is an overbased salicylate of up to 200 conversion. When this salt is treated
5 with zinc, an overbased zinc salicylate is produced.

Zinc Fatty Acid Carboxylates

The essential feature of the carboxylates used in this invention is that they are oil-soluble. The zinc salts of short chain fatty acids, such as acetic, propionic and butyric, are not sufficiently oil soluble to be usable in the compositions of the present
10 invention. The salts of fatty acids containing 8 or more carbon atoms provide the required degree of oil solubility. Specific examples of usable fatty acids include caprylic acid (C₈), capric acid (C₁₀), lauric acid (C₁₂), myristic acid (C₁₄), palmitic acid (C₁₆), stearic acid (C₁₈), oleic acid (unsaturated C₁₈), ricinoleic acid (12 hydroxy oleic acid) and linoleic acid (unsaturated C₁₈). No particular fatty acid is required in
15 the practice of the present invention. Any particular fatty acid may be included or excluded as desired. The zinc salts may be prepared by forming the sodium salt of the carboxylic acid, and reacting that salt with zinc chloride. This replacement reaction may be conducted at a temperature between 100 and 200°C. Zinc carboxylates may also be prepared by saponification of fats using zinc oxide. Zinc
20 carboxylates may also be prepared by the reaction of zinc oxide with carboxylic acids. The reaction is conducted at a moderately elevated temperature to drive off the water formed during the reaction. The moderately overbased zinc carboxylates may be prepared by methods well known to those skilled in the art.

Zinc Salts of the Reaction Product of Glyoxylic Acid and Hydrocarbyl Phenols

The zinc glyoxylates useful in the present invention are zinc salts of the reaction product of glyoxylic acid and hydrocarbyl substituted phenols. These zinc salts correspond to the following formula:



5 wherein Ar is an aromatic group containing 1 to 3 aromatic rings, R is one or more hydrocarbyl groups containing from about 4 to about 150 carbon atoms provided that the number of R groups shall not exceed the available valences on the aromatic group. It is readily apparent from the formula that the zinc salts are the zinc salts of the bis (hydrocarbyl substituted hydroxyaryl) acetic acids produced in the reaction between the glyoxylic acid and the phenol. The phenols used to prepare these salts generally contain aromatic groups (Ar) having no substituents except for the R groups. However, for reasons of cost, and availability, etc., Ar is normally a benzene nucleus.

10 Most preferably Ar is a benzene nucleus substituted by an R group in a position para to the OH group.

Preferably each R is an aliphatic group containing at least 4 and up to about 150 carbon atoms, frequently from about 4 to about 100 carbon atoms, preferably from about 4 to about 75 carbon atoms. In one embodiment, R contains about 4 to about 50 carbon atoms, and in another embodiment from about 4 to about 24 carbon atoms, R is preferably alkyl or alkenyl, preferably substantially saturated alkenyl. Each R may also be an aliphatic group containing about 7 to about 150 carbon atoms, or from about 7 to about 100 carbon atoms, or from about 7 to about 75 carbon atoms, or from about 7 to about 50 carbon atoms, or from about 7 to about 24 carbon atoms, or from about 12 to about 24 carbon atoms. R is preferably alkyl or alkenyl, preferably substantially saturated alkenyl. In one preferred embodiment, R contains at least 7 carbon atoms, often from 12

20

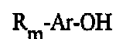
25

to 18 carbons. In another embodiment, each R contains an average of at least 30 carbon atoms, often an average of from about 30 to about 100 carbons. In another embodiment, R contains from 12 to about 50 carbon atoms. In a further embodiment, R contains from about 12 to about 24 carbon atoms and preferably from about 12 to about 18 carbon atoms. For reasons of cost and availability, heptyl, octyl and nonyl-substituted phenols (R = 7 to 9) are a preferred embodiment for this application.

The zinc ions may be derived from zinc metal or reactive zinc compounds that will react with carboxylic acids to form carboxylates such as zinc oxide, zinc hydroxide, zinc carbonate, etc.

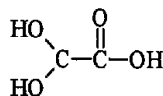
The zinc glyoxylates (zinc salts of the bis (hydrocarbyl substituted hydroxyaryl) acetic acids), which are useful as antiwear agents in the greases of this invention, may be readily prepared by reacting

(a) a reactant of the formula



wherein R is hydrocarbyl containing about 4 to about 150 carbon atoms, m ranges from 1 to about 10, Ar is an aromatic group containing 1 to 3 rings, and m does not exceed the available valences of Ar after allowing for at least one reaction site for the glyoxylic acid to react;

(b) glyoxylic acid shown below as the hydrate



Water of hydration as well as any water generated by the condensation reaction is preferably removed during the course of the reaction.

The reaction is normally conducted in the presence of a strong acid catalyst. Particularly useful catalysts are illustrated by methanesulfonic acid and paratoluenesulfonic acid. The reaction is usually conducted with the removal of water.

Reactants (a) and (b) are preferably present in a molar ratio of about 2:1; however, useful products may be obtained by employing an excess amount of either

reactant. Thus, molar ratios of (a):(b) of 1:1, 2:1, 1:2, 3:1, etc. are contemplated and useful products may be obtained thereby. Illustrative examples of reactants (a) include hydroxy aromatic compounds such as phenols, both substituted and unsubstituted within the constraints imposed on Ar hereinabove, and a variety of aromatic hydroxy compounds. In all the above cases, the aromatic groups bearing the phenolic -OH groups may be single ring, fused ring or linked aromatic groups as described in greater detail hereinabove.

Specific illustrative examples of compounds which may be employed as reactant (a) hydrocarbon-substituted phenols such as di-alkyl phenols, naphthol, 2,2'-dihydroxybiphenyl, 4,4'-dihydroxybiphenyl, 3-hydroxyanthracene, 1,2,10-anthracenetriol, resorcinol, 2-t-butyl phenol, 4-t-butyl phenol, 2,6-di-t-butyl phenol, 2,4-di-t-butyl phenol, octyl phenol, cresols, di-nonyl phenol, propylene tetramer-substituted phenol, propylene oligomer (Mw 300-800)-substituted phenol, polybutene (number average Mw about 1000)-substituted phenol, substituted-naphthols corresponding to the above exemplified phenols, methylene-bis-phenol, bis-(4-hydroxyphenyl)-2,2-propane, and hydrocarbon-substituted bis-phenols wherein the hydrocarbon substituents have at least 4 carbon atoms, for example, butyl, pentyl, hexyl, octyl, dodecyl, oleyl, polybutenyl.

The method of preparation of numerous alkyl phenols is well known. Illustrative examples of alkyl phenols and related aromatic compounds and methods for preparing same are given in U.S. Patent 4,740,321 to Davis et al. This patent is hereby incorporated herein by reference.

U.S. Patents 2,933,520 (Bader) and 3,954,808 (Elliott et al) describe procedures for preparing the reaction product of a phenol and glyoxylic acid. These patents are expressly referred to herein for relevant disclosures relating to preparative procedures and methods contained therein.

The intermediate product obtained from the reaction of the foregoing hydroxy aromatic compounds and carboxylic acids is then reacted with a metal containing reactant to form a salt. Suitable metal-containing reactants have been enumerated hereinabove.

The above examples are intended to be illustrative of suitable reactants and are not intended, and should not be viewed as, an exhaustive listing thereof.

The carboxylate salt is formed by reaction of the metal containing reactant with the glyoxylic acid derivative. The preparation of these salts is described in U.S. Patent
5 5,356,546.

The Zinc salts are effective as antiwear agents at a level from .01% to about 10% by weight of the final grease composition. The preferred amount of the antiwear zinc salt additive is from about 0.25% to about 1%.

Preparation of Greases

10 The methods of preparing urea grease thickeners are well known to those skilled in the art. In a typical preparation, grease compositions may be prepared starting with a base oil of lubricating viscosity and the reactants needed to form an urea thickener. For example, mixture of an amine and the oil is warmed, and the appropriate isocyanate or mixture of isocyanates added. Optionally, the isocyanate
15 may be added as an oil solution. The reaction between the amines and the isocyanates proceeds rather rapidly and generates some heat which is controlled by how much heat is applied to the kettle and the rate of addition of isocyanate. Generally, the reaction between the amines and the isocyanates is conducted at a temperature between about 30 and 70° C. After the urea thickener is formed, a small
20 amount of water is added, and the grease is cooked at a temperature up to about 210° C. The water reacts with any residual diisocyanate. The grease is then cooled, and other desirable additives may be added along with further base oil, if desired. The grease is then milled using an appropriate grease mill to produce the final product. If desired, further additives may be added by reheating the grease and remilling to
25 incorporate these further additives. Variations on this basic process for the formation of urea-thickened greases will be readily apparent to those skilled in the art.

Method of Lubrication

The greases of the present invention may be readily used as lubricants to lubricate metal objects which are in motion relative to one another. In the practice of this method,

the grease of the present invention is placed between the metal objects and provides lubrication and thereby reducing the friction between the metal surfaces as they move with respect to each other. The Lubricant action is provided by the oil of lubricating viscosity. The zinc salts described above, further reduce the friction between the metal surfaces.

5 The urea-thickener serves to thicken the entire composition so that it remains between the metal surfaces rather than flowing out. The amount of grease to be used in this method is determined by the geometry of the metal surfaces to be lubricated. Thus, for example, if the grease is to be used in an automotive roller bearing assembly, the available space in the bearing assembly is packed with grease.

10 All patents referred to herein are expressly incorporated by reference for their relevant disclosures.

The following specific illustrative Examples describe the preparation of the compounds of Formula (I) useful in the compositions of this invention. In the following examples, as well as in the claims and in the specification of this application, parts are

15 parts by weight, the temperature is degrees Celsius and the pressure is atmospheric, unless otherwise indicated.

As will be readily apparent to those skilled in the art, variations of each of the illustrated reactants and combinations of reactants and conditions may be used.

EXAMPLES

20 Example A

Preparation of Zinc Salicylate

800 parts of diluent oil were added to a reactor. 180.8 parts of zinc chloride were added with stirring. 200 parts of water was added. The mixture was warmed to a temperature of 90 - 93°C over one hour. 1000 parts of the sodium salt of an

25 alkylsalicylate (containing xylene 65 to 75% sodium alkyl salicylate), in which the alkyl group contains between 14 and 18 carbons, was added at a temperature of 91-96° C. The batch was held for 2 hours at this temperature. The batch was heated to 154-160°, for a period of 6 hours, while nitrogen was bubbled through the batch to remove aqueous and organic materials. Finally the batch was vacuum-stripped at a

temperature of 154-160° C and a pressure of 20 millimeters of mercury. The product was filtered and the filter flushed using approximately 577 parts of diluent oil. Slightly more or less diluent oil may be used to adjust the product to the desired final concentration. The final water content was less than 0.30%. The product contained
5 30% of the zinc salicylate, and 70% diluent oil.

EXAMPLE 1

A polyurea grease was prepared by reacting 4,4'-methylene biphenyl diisocyanate with a commercial grade of tall oil amine containing predominantly palmityl amine, stearyl amine, and oleyl amine. The amine and the isocyanate were
10 reacted in the base oil at approximately 200°C. The thickened oil was mixed in a grease mill, and the resulting thickened polyurea grease was set aside as a base stock for use in preparing grease samples.

Six grease compositions were prepared starting with a base grease thickened with an urea thickener (results shown in TABLE 1). The greases were subjected to
15 penetration tests and dropping point tests. In addition, they were subjected to the four-ball wear test to determine a scar diameter, as well as the coefficient of friction. Samples 1 through 5 are not examples of the present invention, but instead were prepared with commonly used grease additives. Samples 1-5 are presented for comparison purposes. Sample 6 was prepared according to the present invention.
20 Sample 1 consisted of the base grease mixed with 1% of an additive formed by reacting C₁₄₋₁₈-alcohols with P₂O₅ followed by salting with alkyl C₁₂₋₁₄ primary amines. Sample 2 was formed by adding to the base grease 1% of an additive comprising 76.5% of an amine salt of dithiophosphoric acid, 17.5% of dibutylphosphite, and 6% diluent oil. Sample 3 was formed by adding to the base oil
25 1% of an additive consisting of a calcium overbased sulfonate (TBN = 375) and 50% diluent oil. Sample 4 was formed by adding to the base grease 1% of the additive of Sample 2 and 1% of the additive of Sample 3. Sample 5 was prepared by adding to the base 1% of an additive containing 85% borated soybean lecithin and 15% oil. Sample 6 was prepared by adding to the base grease 1% of an additive, prepared in

Example A, consisting of 30% of the neutral zinc salt of a C₁₄₋₁₈ alkyl salicylic acid and 70% diluent oil.

TABLE 1

Sample ID	Penetration			Dropping	Four-ball Wear	
	UNW	60X	10K	Point	ASTM D2266	
				°C	Scar, mm	Coeff. of Friction
Polyurea base grease Example 1	299	301	306	209	.55	.0907
1	315	310	321	206	.39	.0335
2	304	303	300	203	.44	.0385
3	309	308	319	209	.44	.0400
4	313	306	317	203	.47	.0465
5	315	312	311	208	.39	.0360
6	316	311	321	206	.36	.0285

UNW is the results for the unworked grease.

60X is the results for each grease after 60 strokes.

10K is the results after 10,000 strokes.

EXAMPLE 2

Further grease samples were prepared by adding zinc oleate as an antiwear agent to a commercial sample of a polyurea grease base. The commercial grease base contained a polyurea thickener similar to that prepared in EXAMPLE 1. The base grease served as a control in the tests of the grease. Grease sample 7 was prepared by adding 2 percent zinc oleate to the base grease. Grease sample 8 was prepared by adding 1 percent zinc oleate to the base grease. Grease sample was prepared by

adding 0.5 percent zinc oleate to the base grease. These samples were tested using the a four-ball wear test like that used for EXAMPLE 1. The four-ball wear test was used to determine the coefficient of friction and the scar diameter. The results are shown in TABLE 2. Because the four-ball wear tests were performed at different times, the results are comparable to each other, but not to the results of EXAMPLE 1.

TABLE 2

ITEM NO	CONTROL	7	8	9
% WT				
Polyurea Base Grease	100 %	98 %	99 %	99.5 %
Zinc Oleate		2 %	1 %	0.5 %
ASTM D2266				
Four-ball Wear				
Hours	1	1	1	1
Temp, F	167	167	167	167
RPM	1200	1200	1200	1200
Weight	40 Kg	40 Kg	40 Kg	40 Kg
Avg. Coeff. of Fric.	0.076/0.0900	0.098/0.091	0.06/0.062	0.057/0.058
Avg. Scar Diameter/mm	0.81/0.84	0.57/0.54	0.48/0.51	0.6/0.48

EXAMPLE 3

A zinc glyoxylate (zinc salt of a bis (hydrocarbyl substituted hydroxyaryl) acetic acid) was prepared by reacting 2 moles of dinonyl phenol with 1 mole of glyoxylic acid hydrate in the presence of catalytic quantities of methane sulphonic acid (0.19% by weight). The mixture was vacuum stripped at 110 °C and 35 mm. Hg to remove water. The product was neutralized with potassium hydroxide. The resulting potassium salt was reacted with a stoichiometric amount of zinc chloride to form the zinc glyoxylate. The product contains 60 % neutral zinc glyoxylate, and 40 % diluent oil.

10

EXAMPLE 4

A further grease sample was prepared by adding the zinc glyoxylate (zinc salt of the bis (hydrocarbyl substituted hydroxyaryl) acetic acid) of EXAMPLE B as an antiwear agent to a commercial sample of a polyurea grease base. The commercial grease base contained a polyurea thickener similar to that prepared in EXAMPLE 1. The base grease served as a control in the tests of the grease. Grease sample 10 was prepared by adding 0.67 percent of the zinc glyoxylate of EXAMPLE 3 (containing 0.4 % zinc glyoxylate) to the base grease. The four-ball wear test was used to determine the coefficient of friction and the scar diameter. The results are shown in TABLE 3. Because the four-ball wear tests were performed at different times, the

20

results are comparable to each other, but no to the results of EXAMPLE 1.

Table 3

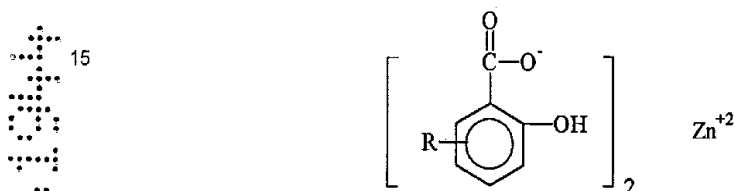
Item No.	Control	10
% WT		
Polyurea Base Grease	100%	99.33%
Zinc Glyoxylate (Ex. 3)		0.67%
ASTM D2266		
Four-ball Wear		
Hours	1	1
Temp, F	167	167
RPM	1200	1200
Weight	40Kg	40Kg
Avg. Coeff. of Friction	0.076/0.0900	0.065
Avg. Scar Diameter/mm	0.81/0.84	0.48

Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification, they are to be interpreted as specifying the presence of the stated features, integers, steps or components referred to, but not to preclude the presence or addition of one or more other feature, integer, step, component or group thereof.



The claims defining the invention are as follows:

1. A grease composition comprising a major amount of an oil of lubricating viscosity and an additive further comprising (A) a thickener selected from the group of mono-ureas, di-ureas, tri-ureas and polyureas and mixtures thereof, and (B) an oil-soluble neutral or overbased zinc salt of a carboxylic acid selected from the group consisting of zinc salts of fatty acids, the zinc salts of hydrocarbyl-substituted salicyclic acids and zinc glyoxylates, provided that if (B) is the zinc salt of a fatty acid, the fatty acid is not ricinoleic acid.
2. A grease composition according to claim 1 wherein the oil-soluble zinc salt comprises an overbased zinc salt.
3. A grease composition according to claim 1 wherein the oil-soluble zinc salt comprises a zinc salt of a hydrocarbyl-substituted salicyclic acid corresponding to the following formula:



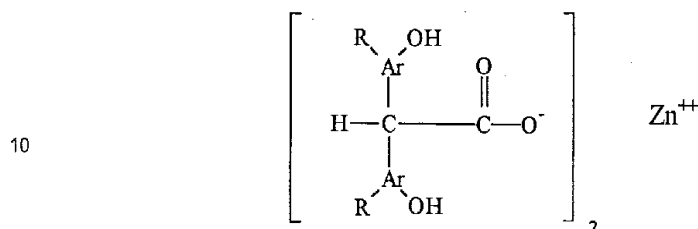
4. A grease composition according to claim 3 wherein the oil-soluble zinc salt comprises an overbased zinc salt of a hydrocarbyl-substituted salicyclic acid.
5. A grease composition according to claim 3 wherein the R group contains between about 7 and 40 carbon atoms.
6. A grease composition according to claim 3 wherein the R group contains between about 7 and 24 carbon atoms.
7. A grease composition according to claim 3 wherein the R group contains between about 12 and 18 carbon atoms.
8. A grease composition according to any one of claims 1 to 7 wherein the oil soluble zinc salt comprises a zinc salt of a fatty acid.
9. A grease composition according to claim 8 wherein the oil soluble zinc salt is selected from group consisting of the zinc salts of caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, and linoleic acid.



10. A grease composition according to claim 8 wherein the oil soluble zinc salt is the zinc salt of oleic acid.

11. A grease composition according to claim 10 wherein the oil soluble zinc salt is an overbased zinc salt of oleic acid.

5 12. A grease composition according to any one of claims 1 to 7 wherein the oil soluble zinc salt comprises a zinc glyoxylate of the following formula:



wherein Ar is an aromatic group containing 1 to 3 aromatic rings, R is one or more hydrocarbyl groups containing from about 4 to about 150 carbon atoms provided that the number of R groups shall not exceed the available valences on the aromatic group.

13. A grease composition according to claim 12 wherein R contains about 4 to about 100 carbon atoms.

14. A grease composition according to claim 12 wherein R contains about 4 to about 50 carbon atoms.

15. A grease composition according to claim 12 wherein R contains about 4 to about 24 carbon atoms.

16. A grease composition according to claim 12 wherein R contains about 7 to about 100 carbon atoms.

17. A grease composition according to claim 12 wherein R contains about 7 to about 50 carbon atoms.

18. A grease composition according to claim 12 wherein R contains about 7 to about 24 carbon atoms.

19. A grease composition about 12 to about 18 carbons atoms.

20. A grease composition according to any one of claims 1 to 19 wherein the thickener comprises a monourea.

21. A grease composition according to any one of claims 1 to 19 wherein the thickener comprises a diurea.

22. A grease composition according to any one of claims 1 to 19 wherein



the thickener comprises a triurea.

23. A grease composition according to any one of claims 1 to 19 wherein the thickener comprises a polyurea.

24. A method of lubricating metal surfaces which move with respect to each other which comprises placing between said metal surfaces an appropriate quantity of a grease composition comprising a major amount of an oil of lubricating viscosity, a thickener selected from the group consisting of monoureas, diureas, triureas and polyureas, and mixtures thereof, and an oil-soluble neutral or overbased zinc salt of a carboxylic acid selected from the group consisting of zinc salts of fatty acids, the zinc salts of hydrocarbyl-substituted salicylic acids, and zinc glyoxylates, provided that if the zinc salt is a zinc salt of a fatty acid, the fatty acid is not ricinoleic acid.

25. A method according to Claim 24, wherein the oil-soluble neutral or overbased zinc salts of a carboxylic acid is a zinc salt of ricinoleic acid.

26. A grease composition according to any one of claims 1 to 23 substantially as hereinbefore described with reference to any one of the Examples.

27. A method according to claim 24 or claim 25 substantially as hereinbefore described with reference to any one of the Examples.

Dated this 29th day of February, 2000.

THE LUBRIZOL CORPORATION

By their Patent Attorneys

CALLINAN LAWRIE

