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(54) Title: USE OF CARBONATES FOR THE REMOVAL OF HCN FROM GAS STREAMS

(57) Abstract

A process for the conversion or oxidation of hydrogen cyanide (HCN) in industrial gas streams, particularly regenerator flue gas from a fluid catalytic cracking (FCC) unit, using solid catalysts comprising carbonates and bicarbonates of Group IA, Group IIA, and Group IIIB elements, e.g., Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, Rb_2CO_3, $CaCO_3$, $SrCO_3$, and $La_2(CO_3)_3$ to convert the HCN to compounds, such as N_2, NO, NH_3, N_2O, HNCO, CO, CO_2, and H_2O.

USE OF CARBONATES FOR THE REMOVAL OF HCN FROM GAS STREAMS

This invention involves the use of solid catalysts containing Group IA, IIA, IIIB, and rare earth carbonates and bicarbonates for the removal of hydrogen cyanide from industrial gas streams.

HCN is known to be present in the flue gas from combustion processes or in exhaust streams from a variety of other industrial sources, including coal combustion and the regeneration of catalysts used in fluid catalytic cracking (FCC) units. HCN is a toxic substance and is believed to contribute to smog formation. In some processes, it may also be a precursor to NO_x formation. NO_x emissions are regulated in many areas.

An FCC regenerator, with or without a CO boiler, can be a very significant contributor to the total NO_x emissions from a refinery. For example, it has been estimated that the FCC regenerator contributes about 45 weight % of the 2000 tons/yr of NO_x released by a typical Southern California refinery. Ideally, all nitrogen species present in the FCC regenerator flue gas would be converted to and would be released into the atmosphere as N_2. Significant quantities of HCN and NH_3 are generally formed in the FCC regenerator only when excess oxygen, i.e. flue gas oxygen, is low. Under these low oxygen conditions, the flue gas from the regenerator will contain from 0.5 to 8 volume % carbon monoxide, which may be converted in a CO boiler. However, in the CO boiler, much or most of the NH_3 and HCN is converted to NO_x.

Before describing the present method for removal of hydrogen cyanide (HCN) from industrial gases, a brief description of thes relevant properties of HCN is in order. HCN is a liquid at atmospheric pressure that boils at 25.7°C and freezes at -13.24°C. It is highly flammable, and burns with a heat of combustion of 159.4 kCal/mol. It forms explosive mixtures with air, and it has unlimited solubility in water. For further description of its physical and chemical properties, including health and safety factors in handling, see "Encyclopedia of Chemical Technology", Kirk-Othmer, Vol. 7, pp. 307-319 (1979).

HCN is hydrolyzed in the presence of an appropriate catalyst to form ammonia by the reaction:

$$HCN + H_2O \longleftrightarrow NH_3 + CO \qquad (1)$$

European Patent 0051156 describes the conversion of HCN to NH_3 over copper oxide, iron oxide, or chromium oxide (Cr_2O_3) at temperatures of between 100° and 500°C; conversions of more than 90% are disclosed. A process is described in Japanese Disclosure 53005065 in which HCN is hydrolyzed to ammonia by at least one oxide of the elements Al, Ce, Zr, Mg, Ca, Ba, Na, K, Mo, V, Fe, Co, Ni, Cu, Mn, Ag, and La. Patent DE-OS 23 41 650 describes a process in which HCN is hydrolyzed with H_2O at temperatures above 93°C in the presence of a catalyst that contains at least an alkali metal hydroxide supported on aluminum oxide, silica, silica-alumina, or a zeolite.

The present invention is directed to a method involving the use of solid catalysts produced from materials comprising Group IA, IIA, IIIB, and rare earth carbonates and bicarbonates, particularly individual or single metal carbonates or bicarbonates, such as sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), potassium carbonate (K_2CO_3), potassium bicarbonate ($KHCO_3$), rubidium carbonate (Rb_2CO_3), calcium carbonate ($CaCO_3$), strontium carbonate ($SrCO_3$), lanthanum carbonate ($La_2(CO_3)_3$) and combinations thereof, for the removal of hydrogen cyanide (HCN) from industrial gas streams, particularly for the oxidation of HCN to compounds such as N_2, NO, NH_3, N_2O, HNCO, CO, CO_2, and H_2O, with conversion to N_2 being desirable due to reduced NO_x emissions. The catalysts of the present invention may comprise a material that is effective to oxidize HCN, but that simultaneously has minimal activity for oxidizing CO to CO_2. One possible example of a catalyst useful in the present invention is a catalyst formed from a material consisting essentially of sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), potassium carbonate (K_2CO_3), potassium bicarbonate ($KHCO_3$), rubidium carbonate (Rb_2CO_3), calcium carbonate ($CaCO_3$), strontium carbonate ($SrCO_3$), lanthanum carbonate ($La_2(CO_3)_3$), supported Na_2CO_3, supported $NaHCO_3$, supported K_2CO_3, supported $KHCO_3$, supported Rb_2CO_3, supported $CaCO_3$, supported $SrCO_3$, supported $La_2(CO_3)_3$, and combinations thereof.

The presently described catalysts are capable of selectively oxidizing the HCN while at the same time oxidizing very little of any CO that is present in the flue gas, thereby preserving the energy that may be produced by combustion of the CO for subsequent recovery in a CO boiler and also reducing the NO_x emissions that may be produced by the CO boiler.

The present invention is based on the discovery that regeneration of fluid cracking catalyst generates a flue gas that may contain small amounts of hydrogen cyanide (HCN) in addition to small amounts of nitric oxide (NO). HCN is known to be present in the flue gas from combustion processes, including coal combustion and FCC catalyst regeneration. It may also be present in exhaust streams from a variety of other industrial sources, such as coke oven gas. HCN is a toxic substance and is believed to contribute to smog formation. In some processes, such as in a CO boiler, it may also be a precursor to NO_x formation. NO_x emissions are regulated in many areas.

Ideally, HCN will be converted by the method of the present invention to N_2, molecular nitrogen, which is the primary constituent of normal air. However, in some cases, the conversion to NH_3 may also be desirable, since ammonia may be easily removed from the gas stream by other means.

According to the method of the present invention, solid catalysts produced from, based upon, or comprising the carbonates or bicarbonates described above may be either added directly to the combustion or HCN-producing process or these catalysts may be used to treat the flue gas after it has left the combustion or reaction zone.

An embodiment of the present invention is a process for the conversion of HCN comprising contacting an industrial gas stream comprising HCN with a solid catalyst produced from a Group IA carbonate, a Group IA bicarbonate, a Group IIA carbonate, a Group IIIB carbonate, including rare earth carbonates, or combinations thereof under conditions effective to convert HCN present in the gas stream to N_2, NO, NH_3, N_2O, or combinations thereof.

Another embodiment of the present invention is a process wherein the solid catalyst mentioned above is added to a combustion zone thereby contacting the solid catalyst with combustion gases formed in the combustion zone under conditions effective to convert HCN present in the combustion gases to N_2, NO, NH_3, N_2O, or combinations thereof.

Although the invention as described herein emphasizes reducing emissions of noxious nitrogen compounds on discharge to the atmosphere of the flue gas from an FCC regenerator, it is contemplated that the invention is broadly applicable to any industrial exhaust gas contaminated by significant quantities of HCN.

The process of the present invention involves the use of solid catalysts produced from or containing carbonates or bicarbonates of the alkali metals, alkaline-earth metals, or rare-earth metals for the removal of hydrogen cyanide (HCN) from gas streams. HCN is known to be present in the flue gas from combustion processes, including combustion of coal or other solid fuel and fluid catalytic cracking (FCC) catalyst regeneration, or in exhaust streams from a variety of other industrial sources, e.g., coke oven gases. The catalysts of the present invention may be either added directly to the combustion zone or HCN-producing process, or they may be used to treat the flue gas after it has left the combustion or reaction zone.

Unexpectedly, the method of the present invention is suitable to oxidize HCN with a high conversion of the HCN, e.g., at least 90 weight percent of the HCN is converted, e.g., at least 95 weight percent of the HCN is converted, e.g., at least 98 weight percent of the HCN is converted, based upon the feed and product from the catalytic zone of the present invention. Also unexpectedly, the method of the present invention produces a high selectivity to the production of elemental nitrogen, N_2, e.g., a selectivity of at least 30 percent, e.g., at least 35 percent, e.g., at least 50 percent, e.g., at least 60 percent, e.g., at least 75 percent, e.g., 80 percent or higher. It is also unexpected that the present catalyst displays little or no activity for conversion of CO to CO_2 under the conditions employed to convert HCN, for example conversion levels of less than 10 weight percent, e.g., less than 5 weight percent, e.g., less than 2 weight percent of the CO based upon feed and product from the catalytic zone of the present invention.

Ideally, HCN will be converted to molecular nitrogen, N_2, which is the primary constituent of normal air. However, in some cases, the conversion to NH_3 may also be desirable, since ammonia may be easily removed from the gas stream by other means.

When the catalyst of the present invention is used to treat flue gas from combustion processes, e.g., flue gas from FCC catalyst regeneration, the catalyst of the present invention may be located after the last catalyst separation stage and before any CO boiler or other heat recovery stage. A suitable location is one where the temperature of the flue gas is 400 to 875°C or higher, e.g., 400 to 800°C, e.g., 500 to 700°C. The catalyst of the present invention is particularly suitable for use ahead of a CO boiler because it is selective for the conversion of HCN and has little or no activity for the oxidation of carbon monoxide, CO, under suitable HCN conversion conditions.

Another possible location for use of the catalyst of this invention includes the use of this catalyst in a solid fuel combustion zone, such as would be found in the FCC regenerator itself or a solid fuel combustor such as a circulating fluid bed boiler or a fixed-fluid bed boiler or even in a hybrid system which has some entrainment. In this embodiment, the solid catalyst is added, either separately or with the solid fuel, e.g., sulfur-containing coal, to the combustion zone, where the solid fuel is combusted to produce a combustion gas and frequently to produce an ash, such as coal ash. The solid catalyst of the present invention circulates through the solid fuel combustor with the other solids that are present, such as FCC catalyst or coal ash and including any inerts that are used to control flow, mixing and temperature patterns in the combustor. In the combustion zone, the solid catalyst contacts the combustion gas to convert the HCN that is present in the combustion gas as described herein. After passing through the combustion zone, the solid catalyst may be separated from the other coarse solids using well known solids separation techniques, such as screening, density separation or other methods. A portion of the solid catalyst, e.g., a substantial portion of the solid catalyst, may be directly returned to the combustion zone. The combustion gas after the HCN conversion, containing among other compounds, one or more of N_2, NO, NH_3, N_2O, HNCO, CO, CO_2, and H_2O, may be directed to other treatment units for conversion of the unwanted components in the gas, such as a CO boiler, selective catalytic reduction unit, scrubber or water wash unit.

Current circulating fluid bed combustors are operated at 840°C to 875°C because that is an effective temperature range for SO_x uptake by limestone ($CaCO_3$). The solid catalysts of this invention are effective for HCN conversion at much lower temperatures, as low as 500°C, although they are also effective up to 875°C or higher. Because carbon combustion may become undesirably slow at temperatures below 650°C, a range of operation for this embodiment is therefore 650°C to 850°C in certain solid fuel combustors, e.g., coke or coal fired combustors, and

650°C to 760°C in other solid fuel combustors, e.g., FCC regenerators.

The solid catalyst of this invention is suitable for use with bubbling bed and high efficiency FCC regenerators, as are known in the art.

Catalyst

Suitable solid catalysts for the process of the present invention include catalysts produced from carbonates and bicarbonates of the alkali metals, the alkaline-earth metals, and the rare-earth metals, e.g., the single metal or individual metal carbonates and bicarbonates of Group IA, e.g., Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$ and Rb_2CO_3; Group IIA, e.g., $CaCO_3$ and $SrCO_3$; and Group IIIB, such as rare earth carbonates, e.g., $La_2(CO_3)_3$, of the Periodic Table of the Elements as specified in the Handbook of Chemistry and Physics, 61st ed., CRC Press, 1980-1981. These catalysts may be formed from the carbonates or bicarbonates themselves, may be formed from compounds that produce the desired carbonates or bicarbonates, such as by dissolving water soluble salts of the desired alkali metal, alkaline-earth metal, or rare-earth metal and then adding a water soluble carbonate salt, e.g., sodium carbonate to form a precipitate containing the desired carbonate, or may include a suitable support for the carbonates and bicarbonates.

Sodium carbonate (soda ash) may be produced by several well-known processes, such as the Solvay (ammonia-soda) process and the natural soda process, such as from trona or brine. The carbonates of the present invention may be prepared in any form that is suitable for use in the present process, e.g., they may be in their hydrated or anhydrous form. Under the conditions present in the present process, some or all of the bicarbonate may convert to carbonate, and some or all of the carbonates mentioned above, may decompose, however any decomposition products thus formed are catalytically active for the present reaction.

Sodium carbonate, produced as mentioned above, may contain one or more impurities, such as iron, however, the catalysts of the present invention do not include intentionally added materials, such as nickel, zinc, or iron. The catalysts of the present invention may be free of intentionally added transition metals, such as Group VIII metals.

The concentration of the carbonates or bicarbonates in the catalysts may range from 1/2 or 1 weight percent to 100 percent, e.g., 2 to 75 weight percent, e.g., 5 or 10 weight percent to 50 weight percent, e.g., 5 to 30 weight percent, with reference to the weight of the total catalyst composition. The catalysts may be formed by incipient wetness impregnation of the support using an aqueous or other suitable solution of the carbonate or bicarbonate desired or by using suitable precursors of the desired carbonate or bicarbonate. For example, water insoluble carbonates may be dissolved in dilute acid solutions, e.g., in dilute nitric acid. Naturally, other methods that are known in the art may be used for combining the desired carbonate or bicarbonate with the support, such as physically mixing or mulling the materials together and then forming them into the desired shapes, e.g., by extrusion, spray drying or pelleting.

As mentioned above, it may be desired to support or to incorporate the catalyst of this invention with another material resistant to the temperatures and other conditions employed in the present HCN conversion process. Such materials may include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and/or metal oxides such as alumina, titania and/or zirconia. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. These materials may be incorporated with naturally occurring clays, e.g. bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions. Said materials, i.e. clays, oxides, etc., function as supports or binders for the catalyst. It is desirable to provide a catalyst having good crush strength because in commercial use it is desirable to prevent the catalyst from breaking down into powder-like materials.

In addition to the foregoing materials, the catalyst of this invention can be supported or composited with a porous matrix material such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia.

The form and the particle size of the support and resulting catalyst are not critical to the present invention and may vary depending, for example, on the type of reaction system employed.

Process Conditions

The process of the present invention contacts an industrial gas containing hydrogen cyanide (HCN) with the solid catalysts described above under conditions effective to convert or oxidize a substantial amount of HCN present in the industrial gas to other compounds, such as N_2, NO, NH_3, N_2O, HNCO, CO, CO_2, and H_2O. The process of the present invention is capable of selectively converting HCN in the presence of carbon monoxide, CO, without converting or oxidizing CO. In particular, the process of the present invention is capable of converting a higher percentage of HCN in the gas than the percentage of CO that is converted. In other words, according to the process of the present invention, the ratio of the proportion of HCN present in the gas stream that is oxidized to the proportion of CO present in the gas stream that is oxidized may be at least 2, e.g., at least 5, e.g., at least 10. Further, when the present catalysts contact the HCN containing gas under the conditions identified herein, the catalysts have no increased nitrogen contents, i.e., there is no adsorption, absorption, or chemical reaction of the nitrogen compounds present in the gas on or with the catalysts of the present invention.

A source of oxygen is frequently present in, is included with, or is added to the gas stream to be treated. Further, a small amount of water vapor is frequently present or is included in the gas stream to be treated.

Some conversion conditions that may be used in the present invention include a temperature of from 400°C to 875°C or higher, e.g., 450°C to 800°C, e.g., 500°C to 700°C, a pressure of from 10 psia (69 kPa) to 200 psia (1379 kPa), and a gas hourly space velocity of from 2000 to 100,000 hr^{-1}, e.g., 5000 to 50,000 hr^{-1}.

Example 1

Experiments were conducted in which gas streams containing HCN, O_2, and H_2O (metered from cylinders of known concentration) were passed over a catalyst bed containing selected carbonates, bicarbonates or supported carbonates. These experiments show that HCN can be converted to N_2 over a variety of catalyst preparations across a wide range of temperatures. At all temperatures, some byproducts, including NO, NH_3, and N_2O were formed. These byproducts could be removed, if necessary, by further treatment of the gas stream.

Table 1 shows the data collected over several catalysts in the temperature range of 500 to 700°C. In these experiments, the inlet HCN concentration was maintained at 100 or 80 ppm by volume, the inlet oxygen concentration was maintained at 1 % by volume, and the inlet water (as water vapor) concentration was maintained at approximately 0.5 % by volume; the balance of the gas stream was argon. The total gas flowrate was 400 cm^3/min and one gram of catalyst was used, producing a gas hourly space velocity of 24,000 hr^{-1}. Where supported catalysts are indicated, the catalysts were prepared by incipient wetness impregnation, although other methods would be included within the scope of the present invention. Where the supported catalysts were prepared from water insoluble carbonates, the carbonates were dissolved in dilute nitric acid and incipient wetness impregnation was used. The catalysts were dried for two hours at 120°C in air, pelletized, crushed, and sized to 20/40 mesh. Densities of the catalysts varied, with the silica-supported catalysts having packed densities of 0.7 to 1 g/cm^3, as did $NaHCO_3$, while the Na_2CO_3, $CaCO_3$, and $La_2(CO_3)_3$ catalysts had packed densities of about 2 g/cm^3. HCN, NH_3, NO, N_2O, CO, and CO_2 concentrations were measured by infrared spectroscopy and the N_2 concentration was calculated by a mass balance. Elemental analysis of the catalysts before and after the experiment showed no increase in nitrogen content.

Table 1

Catalyst	Temperature °C	Inlet HCN ppm	Conversion %	NO ppm	NH_3 ppm	N_2O ppm	N_2 ppm	Selectivity to N_2, %
Na_2CO_3	500	100	100	23	7	2	33	66
10% Na_2CO_3/SiO_2	600	100	98	12	55	0	16	32
10% Na_2CO_3/SiO_2	700	100	100	8	14	0	39	78
30% Na_2CO_3/SiO_2	500	100	100	32	28	3	17	34
30% Na_2CO_3/SiO_2	600	100	100	36	23	2	19	37
30% Na_2CO_3/SiO_2	700	100	99	8	50	0	21	41
$NaHCO_3$	500	100	100	11	13	1	37	74
$NaHCO_3$	600	100	100	27	12	2	29	57
$NaHCO_3$	700	100	100	25	8	0	34	67
10% K_2CO_3/SiO_2	700	100	100	18	35	1	24	48
30% Rb_2CO_3/SiO_2	700	100	98	10	7	1	40	82
$CaCO_3$	700	100	100	49	13	0	19	38
$La_2(CO_3)_3$	700	100	100	55	3	0	21	42
20% $La_2(CO_3)_3/SiO_2$	700	80	100	23	23	1	17	40
10% $CaCO_3/SiO_2$	700	80	100	24	1	1	27	68
20% $SrCO_3/SiO_2$	700	80	100	35	3	1	20	50

Example 2

The catalyst was prepared by incipient wetness impregnation of silica (SiO_2) with 10 weight percent sodium carbonate (Na_2CO_3) in an aqueous solution in a fashion similar to that of Example 1. Table 2 shows the data collected over this catalyst in the temperature range of 400 to 650°C. In these experiments, the inlet HCN concentration was maintained at 100 ppm by volume, the inlet oxygen concentration was held at 1 % or 0.5 % by volume, the inlet CO concentration was maintained at 1.0 % by volume, and no ammonia was added to the gas stream; the balance of the gas stream was argon. The total gas flowrate was 400 cm^3/min and one gram of catalyst was used, producing a gas hourly space velocity of 24,000 hr^{-1}.

Table 2

Temp., °C	At 1 % O_2 Conversion CO, %	HCN-N_2, %	Total	At 0.5 % O_2 Conversion CO, %	HCN-N_2, %	Total
400	0	43	55	0	12	19
450	2	58	99	1	52	100
500	2	66	100	1	65	100
550	2	74	100	0	72	100
600	1	78	100	1	80	100
650	2	75	100	1	78	100

WHAT IS CLAIMED IS:

1. A process for the conversion of HCN comprising contacting an industrial gas stream comprising HCN with a solid catalyst produced from a Group IA carbonate, a Group IA bicarbonate, a Group IIA carbonate, a Group IIIB carbonate, or combinations thereof under conditions effective to convert HCN present in the gas stream to N_2, NO, NH_3, N_2O, or combinations thereof.

2. The process according to claim 1, wherein the industrial gas stream is contacted with the solid catalyst by adding the solid catalyst to a solid fuel combustion zone which produces the industrial gas stream.

3. The process according to claims 1 and 2, wherein the solid catalyst is produced from a material comprising a single metal carbonate or bicarbonate.

4. The process according to claims 1 and 2, wherein the solid catalyst is free of intentionally added transition metal.

5. The process according to claims 1 and 2, wherein the solid catalyst is produced from Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, Rb_2CO_3, $CaCO_3$, $La_2(CO_3)_3$, $SrCO_3$, supported Na_2CO_3, supported $NaHCO_3$, supported K_2CO_3, supported $KHCO_3$, supported Rb_2CO_3, supported $CaCO_3$, supported $La_2(CO_3)_3$, supported $SrCO_3$, or combinations thereof.

6. The process according to claim 5, wherein the support for the solid catalyst comprises silica.

7. The process according to claims 1 and 2, wherein the conversion conditions comprise a temperature of from 400°C to 875°C, a pressure of from 10 (69 kPa)to 200 psia (1379 kPa), and a gas hourly space velocity (GHSV) of from 2000 to 100,000 hr^{-1}.

8. The process according to claims 1 and 2, wherein at least 90 percent of the HCN is converted and wherein less than 10 percent of any CO present in the gas stream is oxidized to CO_2.

9. The process according to claims 1 and 2, wherein the industrial gas stream is selected from the group consisting of fluid catalytic cracking unit regenerator flue gas, coke oven gas, and exhaust gas from a solid fuel combustion process.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/18288

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01D 53/54; C10G 11/00
US CL :423/236,239.1; 208/113,120
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/236,239.1; 208/113,120

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,668,491 A (WIMMER et al) 26 May 1987, col. 5, line 60- col. 6, line 13.	1-2, 5, 8
Y	US 5,173,278 A (MARLER et al.) 22 December 1992, col. 1, lines 23-55, col. 2, lines 39-69, col. 3, lines 1-15 and 41-46.	1-3, 5, 8
Y	US 5,240,690 A (TANG et al) 31 August 1993, col. 3, lines 25-64, col. 4, lines 2-35.	1-3, 5, 8
X	US 3,034,932 A (DONOVAN et al) 15 May 1962, col. 1, lines 1-60 and col. 4, lines 1-60.	1, 4-5, 7-8
X	US 5,364,517 A (DIECKMANN et al) 15 November 1994, col. 1, lines 34-69, col. 4, lines 3-20, col. 12, line 19.	1, 5-6, 8-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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