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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

I\We,

MITSUBISHI GAS CHEMICAL COMPANY, INC.

of

2-5-2, MARUNOUCHI, CHIYODA-KU
TOKYO
JAPANhereby apply for the grant of a standard patent for an
invention entitled:COMPOUNDS USING
AN ANHYDROUS HYDROGEN FLUORIDE
CATALYST--.

which is described in the accompanying complete specification

Details of basic application(s):

Number of basic application	Name of Convention country in which basic application was filed	Date of basic application
191521/85	JP	31 AUG 85

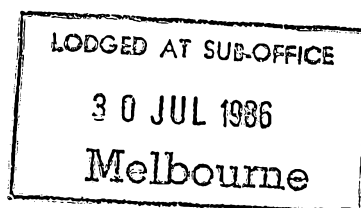
My/our address for service is care of CLEMENT HACK & CO., Patent
Attorneys, 601 St. Kilda Road, Melbourne 3004, Victoria,
Australia.

DATED this 30th day of July 1986

MITSUBISHI GAS CHEMICAL
COMPANY, INC.

CLEMENT HACK & CO.

TO: The Commissioner of Patents.

g7 M. t.

APPLICATION ACCEPTED AND AMENDMENTS
 22-1-86
 ALLOWED

CLEMENT, HACK, & CO.

1829872
(#21-117)
Australia Patent Declaration Form

Forms 7 and 8

AUSTRALIA

Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION

Name(s) of Applicant(s) In support of the application made by MITSUBISHI GAS
CHEMICAL COMPANY, INC.,

Title for a patent for an invention entitled "PROCESS FOR
PRODUCING ACETYL-SUBSTITUTED AROMATIC COMPOUND"

Name(s) and address(es) of person(s) making declaration I/We, Wakichi NAGANO, c/o MITSUBISHI GAS CHEMICAL
COMPANY, INC., of 5-2, Marunouchi-2-chome, Chiyoda-ku,
Tokyo, Japan,

do solemnly and sincerely declare as follows:-

1. I am/we are the applicant(s) for the patent, or
am/are authorised by the abovementioned applicant
to make this declaration on its behalf.

2. The basic application(s) as defined by Section 141
of the Act was/were made in the following country
or countries on the following date(s) by the
following applicant(s) namely:-

Country, filing
date and name
of Applicant(s)
for the or
each basic
application

Country, filing
date and name
of Applicant(s)
for the or
each basic
application

in Japan on August 31, 19 85
by MITSUBISHI GAS CHEMICAL COMPANY, INC.
in _____ on _____ 19 ____
by _____

3. The said basic application(s) was/were the first
application(s) made in a Convention country in respect
of the invention the subject of the application.

Name(s) and
address(es)
of the or
each actual
inventor

Name(s) and
address(es)
of the or
each actual
inventor

4. The actual inventor(s) of the said invention is/are
Susumu FUJIYAMA, Shunichi MATSUMOTO and Tatsuhiko YANAGAWA,
of: 522-65, Kamitomi, Kurashiki-shi, Japan;
1168-3, Tanoue, Kurashiki-shi, Japan; and
1987, Nakashima, Kurashiki-shi, Japan.

5. The facts upon which the applicant(s) is/are entitled
to make this application are as follows:-

See reverse
side of this
form for
guidance in
completing
this part

The said applicant is the assignee of the said
actual inventors.

DECLARED at Tokyo, Japan this 18th day of July, 19 86.

MITSUBISHI GAS CHEMICAL COMPANY, INC.

Wakichi Nagano
Wakichi NAGANO
President

(12) PATENT ABRIDGMENT (11) Document No. AU-B-60713/86
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 595523

(54) Title
ACETYLATION OF AROMATIC COMPOUND WITH ACETYL FLUORIDE

International Patent Classification(s)
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(56) Prior Art Documents
AU 44626/85 C07C 49/825
FR 2348181

(57) Claim

1. A continuous process for producing an acetyl-substituted aromatic compound using an anhydrous hydrogen fluoride catalyst which comprises
 obtaining an acetyl fluoride by the reaction of excess acetic anhydride with an anhydrous hydrogen fluoride wherein the ratio of excess acetic anhydride to hydrogen fluoride is 5 mol% or below, and separating formed acetyl fluoride by distillation,
 reacting an aromatic compound selected from alkyl-benzenes, alkyl-naphthalenes, phenols, naphtholes or aromatic ethers with the separated acetyl fluoride in the presence of anhydrous hydrogen fluoride as a catalyst, and
 thermally decomposing the resulting complex compound between the acetyl-substituted aromatic compound and hydrogen fluoride in the presence of a solvent which is inert to hydrogen fluoride.

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Form 10

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

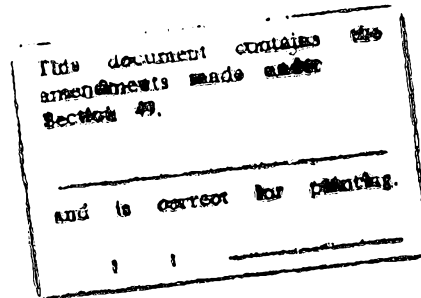
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TO BE COMPLETED BY APPLICANT

Name of Applicant:

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Australia.

Complete Specification for the invention entitled:
COMPOUNDS USING
AN ANHYDROUS HYDROGEN FLUORIDE
CATALYST--.

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



1 BACKGROUND OF THE INVENTION

This invention relates to a process for producing an acetyl-substituted aromatic compound which comprises acetylating an aromatic compound such as an aromatic
5 hydrocarbon ~~and~~^{or} a phenol with acetyl fluoride.

It is disclosed in Japanese Patent Application Kokai (Laid-open) No. 135756/79 to produce a 2-alkyl-6-acylnaphthalene by acylating a 2-alkylnaphthalene with an acid fluoride in the presence of boron fluoride or
10 hydrogen fluoride and boron fluoride as a catalyst.

It is described in the above-mentioned invention that the presence of boron fluoride as a catalyst component is essential and the absence of boron fluoride results in low yield of the acylation product. However,
15 according to the experiment of the present inventors, it has been found that when boron fluoride is used as a catalyst component in the reaction of aromatic compound with acetyl fluoride, it is difficult to decompose the resulting complex compound on account of the instability
20 of aromatic keton of the reaction product.

SUMMARY OF THE INVENTION

Accordingly, the present inventors have made extensive studies to attain a process for producing an acetyl-substituted aromatic compound with higher efficiency



1 including the steps of the decomposition of the complex
compound and the recovery of the catalyst component.
Consequently, it has been found that, in the reaction
of an aromatic compound with acetyl fluoride, even when
5 hydrogen fluoride alone is used as a catalyst the intended
acetyl-substituted aromatic compound can be obtained
in excellent yield and further the complex compound formed
can be readily decomposed and the hydrogen fluoride
catalyst can be easily recovered. This invention has
10 been accomplished on the basis of ^{the} above findings.

DETAILED DESCRIPTION OF THE INVENTION

Thus, this invention provides a process for
producing an acetyl-substituted aromatic compound which
comprises making an aromatic compound including an 2-
15 alkylnaphthalene react with acetyl fluoride in the
presence of ~~substantially~~ anhydrous hydrogen fluoride
as a catalyst.

The aromatic compounds used as the starting
material in this invention include alkylbenzenes such as
20 toluene, xylene, trimethylbenzene, ethylbenzene, cumene,
and butylbenzene; naphthalene and alkylnaphthalenes
such as methylnaphthalene; phenols and naphthols; and
further aromatic ethers such as anisole and phenyl ether.
Particularly preferred are compounds in which the para
25 position to the substituent in the aromatic ring is
vacant and naphthalenes having a substituent in the
2-position.



1 and hydrogen fluoride are fed to the appropriate plate
of the distillation column as a mixture or separately,
the column bottom is heated up to the boiling point of
the acid and the column top is given an appropriate
5 reflux. Such a conventional distillation operation
makes it possible to recover pure acetyl fluoride from
the column top and an acid containing no fluorine from
the column bottom.

Since the reaction proceeds at a high rate,
10 virtually no residence time is necessary. The reaction
can be conducted under an ^{atmospheric} ~~ordinary~~ or an applied pressure,
for example $1 \text{ kg/cm}^2 \text{G}$, and either flow operation or
batchwise operation may be used. The difference of
boiling point between acetyl fluoride and the acid
15 formed is so large that the two can be easily separated.

The acetyl fluoride thus formed is used for
acetylation as the acetylating agent. The molar ratio
of acetyl fluoride to the starting aromatic compound
is, ^{preferably} 1 or below, 0.9 to 0.5 being particularly preferable.
20 The presence of excess acetyl fluoride decreases the
overall reaction rate (i.e. the space time yield of the
acetylation product).

As the catalyst, ~~a substantially~~ ^{an} anhydrous
hydrogen fluoride is used. Its water content is
25 preferably 5% or below because the presence of water in
hydrogen fluoride causes the rapid decrease of catalytic
activity. In order to obtain a sufficient reaction rate,
the molar ratio of hydrogen fluoride to be used relative



to the acetylating agent is preferably 5 or above, being particularly preferable in the range of 10 to 20. Hydrogen fluoride used in a molar ratio of 20 or above gives little additional effect and hence is not
5 advantageous from the economical viewpoint of the process.

The reaction temperature of acetylation is preferably 0 to 70°C, being particularly preferable between 10 to 50°C. Since the reaction rate increases as
10 the temperature is increased but also the side reaction increases, an optimum temperature is selected from the above-mentioned range depending upon the starting material used. When the starting compound has a high melting point and further is insoluble in hydrogen
15 fluoride as in the case of aromatic hydrocarbons, it is effective to use a suitable solvent in order to make the reaction proceed smoothly. Preferably solvents are those which can dissolve the starting compound well, are chemically inert under reaction conditions, and have a
20 good compatibility also with the reaction liquid formed. They include, for example, benzene or halogenated hydrocarbons such as chlorobenzene, dichloromethane, dichloroethane and freon. Particularly, benzene is the most suitable solvent in the present process because it
25 is not only substantially inert under the present reaction conditions but also favourable as the solvent in the step of recovering the catalyst from the reaction mixture.

The amount of the solvent to be used in the
30 reaction is not specifically limited. The amount of



1 0.5 mole or below per mole of the starting compound is usually sufficient.

Although the reaction pressure is varied depending on the reaction temperature, usually it ranges
5 from ~~an ordinary~~ ^{atmospheric} pressure to a slightly elevated pressure of up to 2 kg/cm²G.

The reaction proceeds in a homogeneous liquid phase or, according to circumstances, in two-liquid phases consisting of a starting aromatic compound phase
10 and a catalyst phase, so that there is no need of vigorous stirring. Since the reaction is slightly exothermic, a reactor provided with heat removal equipment is used as required.

The acetylation reaction liquid thus obtained
15 is a solution of an aromatic ketone, the acetylation product, in hydrogen fluoride. On heating the reaction liquid, the affinity between the reaction product and hydrogen fluoride is broken and hydrogen fluoride can be easily vaporized and separated.

20 It is necessary to conduct the above-mentioned catalyst recovery operation as rapidly as possible in order to avoid the thermal degradation of the reaction product. For this purpose, the catalyst recovery operation is preferably conducted in a flow operation
25 using a multistage gas-liquid contact apparatus (i.e. a distillation column). For catalyst recovery, heating at a temperature of 40°C or higher, particularly 40 to 100°C, is necessary. The decomposition column is



1 preferably fed with an amount of heat which is in excess
of that necessary for vaporizing hydrogen fluoride fed
to the column. It is advantageous in the process to
conduct the catalyst recovery operation under atmospheric
5 pressure or a slightly increased pressure of $2 \text{ kg/cm}^2\text{G}$
or below. In order to make the thermal decomposition
of the complex compound between the acetyl-substituted
aromatic compound and hydrogen fluoride proceed smoothly,
the decomposition is preferably conducted by heating
10 the complex compound under reflux using as a diluent a
substance which has a boiling point such that it is
easily separable from hydrogen fluoride, has a good
compatibility with the reaction product, namely the
acetyl-substituted aromatic compound, and with hydrogen
15 fluoride, and is inert to hydrogen fluoride. Examples
of such diluent used include aromatic compounds such
as benzene and chlorobenzene. Particularly, benzene is
the most preferable.

According to this invention, aromatic compounds
20 can be acetylated in a simple operation under low reaction
pressure, and hydrogen fluoride used as the catalyst
can be completely recovered and recycled. So this
invention is of great industrial advantage.

The accompanying drawing is a flow diagram
25 showing the acetylation process of this invention.

The process for acetylating an aromatic
compound according to this invention is illustrated below
with reference to Fig. 1.

1 In Fig. 1, acetic anhydride is fed to the
middle plate of an acetyl fluoride generating apparatus
2 through pipe 1 and contacted there with heating with
hydrogen fluoride introduced through a pipe 3. The
5 acetyl fluoride formed is distilled out through an
outlet pipe 4 and acetic acid is withdrawn through a
pipe 5. The acetyl fluoride is fed to an acetylation
reactor 6 equipped with a stirrer 19 and is contacted
there with stirring with the starting aromatic compound
10 fed through a pipe 7 and with hydrogen fluoride fed
through a pipe 8. The reaction begins in two liquid
phases of the hydrogen fluoride phase and the starting
material oil phase, which then change into a homogeneous
liquid phase as the reaction proceeds. The reaction
15 liquid is drawn out through a pipe 9, led to a hydrogen
fluoride recovery column 10, and contacted there with
a diluent such as benzene which is being refluxed and
recycled. Hydrogen fluoride is separated by vaporization
and drawn out through a pipe 11. The column top vapor
20 is condensed by cooling and separated into layers. The
benzene phase is refluxed from a pipe 12 to the recovery
column 10; hydrogen fluoride is recycled to the acetyl
fluoride generating apparatus and the acetylation
reactor (not shown in the Figure). From the bottom of
25 the hydrogen fluoride recovery column is withdrawn
through a pipe 13 the acetylation product, a crude product,
which is then freed from trace amount of residual acid in
a neutralization and washing equipment 14 and distilled

1 in a distillation apparatus 15, whereby the byproduct
is removed through a pipe 16, the unreacted raw material
is removed through a pipe 17 to be recycled to the
reaction step, and the final product is obtained through
5 a pipe 18.

A suitable solvent is used to make the reaction
proceed smoothly as required. This is added to the
starting material in a pipe 7. Fig. 1 shows a case
where the solvent and the diluent for decomposition are the
10 same. But, in the case where both are different, further
a process for recovering the solvent is added to it.

This invention will be further explained in
detail below with reference to Examples, but it is not
limited thereto.

15 Example 1

Synthesis of acetyl fluoride

A stainless steel packed column having a
diameter of 50 mm and a height of 1000 mm provided with
a top reflux apparatus and a bottom reboiler was used
20 as the acetyl fluoride synthesizer. Acetic anhydride
(22.0 moles per hour) and hydrogen fluoride (21.0 moles
per hour) were mixed and fed continuously to the middle
plate of the packed column, and heat was supplied to the
reboiler with an electric heater at a rate of 260 Kcal
25 per hour. The synthesizer was operated under a pressure
of 1.0 kg/cm²G. While reflux was applied so as to keep
the temperature of the column top at about 35°C, acetyl

1 fluoride was distilled out of the column top at a rate
of 21 moles per hour, and a liquid mixture comprising
21 moles of acetic acid and 1 mole of acetic anhydride
was withdrawn every hour from the bottom. The yield of
5 acetyl fluoride relative to supplied hydrogen fluoride
was quantitative.

Acetylation of 2-methylnaphthalene

Two stainless steel vessels each equipped with
a stirrer, the first reactor having an inner liquid
10 volume of 6 l and the second reactor having an inner
liquid volume of 4 l, were connected in series to be
used as the acetylation reactor. A solution comprising
1.5 kg of 2-methylnaphthalene and 0.3 kg of benzene
was fed every hour to the first reactor. Simultaneously,
15 0.5 kg per hour of acetyl fluoride synthesized above
and 2.5 kg per hour of hydrogen fluoride were also fed
to the first reactor.

The reaction temperature was adjusted to 25°C
by passing cooling water through the jacket of the
20 reactor. The pressure in the reaction was 1 kg/cm²G.
The reaction mixture was continuously withdrawn from
the second reactor to be fed to the subsequent hydrogen
fluoride recovery column.

Recovery of hydrogen fluoride

25 The packed column used in acetyl fluoride
synthesis was employed as the hydrogen fluoride recovery

1 column. The hydrogen fluoride recovery column was charged with benzene, and heat was supplied at a rate of 300 Kcal per hour to the reboiler under a pressure of 1 kg/cm²G to keep the benzene refluxing.

5 Then the above-mentioned reaction mixture was continuously fed to the upper part of the column at a rate of 1 kg per hour, and the hydrogen fluoride recovery column was continuously operated while being replenished with benzene.

10 From the column top were distilled out hydrogen fluoride and unreacted acetyl fluoride, while from the column bottom were recovered every hour 243 g of acetylated methylnaphthalene, 109 g of unreacted methylnaphthalene, and 20 g of a high boiling point
15 product as the crude acetylation product. The acetylation product contained 75% of 2-acetyl-6-methylnaphthalene.

Example 2

Acetylation of toluene

20 Toluene was acetylated by using the same apparatus and the same operation as in Example 1.

To the first reactor were fed every hour 0.9 kg of toluene, 0.4 kg of acetyl fluoride, and 2.0 kg of hydrogen fluoride, and the reaction was conducted at a reaction temperature of 40°C and under a reaction
25 pressure of 1.5 kg/cm²G. The reaction mixture was continuously withdrawn from the second reactor and hydrogen fluoride was recovered in the same manner as in

1 Example 1. The crude product obtained from the bottom
of the hydrogen fluoride recovery column had the
following composition: unreacted toluene 55%, methyl-
acetophenone 41%, high boiling point product 4%. The
5 methylacetophenone contained 97.5% of 4-methylacetophenone.

Example 3

Acetylation of m-xylene

A stainless steel autoclave of 500 ml volume
equipped with a jacket and a stirrer was used as the
10 acetylation reactor.

A solution of 56 g (0.9 mole) of acetyl
fluoride in 103.1 g (1 mole) of m-xylene was placed in
the autoclave, and then, with cooling, 300 g (15 moles)
of hydrogen fluoride was introduced thereinto. The
15 mixture was allowed to react at a reaction temperature
of 40°C under a reaction pressure of 1.5 kg/cm²G for
1.5 hours. Thereafter, the reaction mixture was withdrawn
into ice water. The resulting oil layer was washed with
alkaline water and distilled to determine the amount of
20 high boiling point byproducts and analyzed by gas
chromatograph to determine the yield of the acetylated
product.

Examples of acetylations conducted in the same
manner as mentioned above using various aromatic compounds
25 as the starting material are summarized in Table 1.

Table 1

Starting aromatic compound (A)	Acetylation conditions				Acetylation yield relative to (A) (mol %)
	Molar ratio		Temperature (°C)	Time (hour)	
	ACF/(A)	HF/ACF			
2-Methylnaphthalene	0.75	16	25	2	60
Toluene	0.65	15	40	3	33
m-Xylene	0.9	15	40	1.5	75
Mesitylene	0.9	10	40	1.5	82
Isobutylbenzene	0.7	15	40	4	40
Phenol	0.9	20	25	3	82
Anisole	0.95	20	25	2	89
Phenyl ether	0.8	20	25	2	71

to be continued

Table 1 (cont'd)

High-boiling byproduct relative to acetylation product (wt.%)	Composition of acetylation product (Gas chromatographic analysis)
8	2-Acetyl-6-methylnaphthalene 75%
10	4-Methylacetophenone 97.5%
7	2,4-Dimethylacetophenone 100%
7	2,4,6-Trimethylacetophenone 100%
4	p-Isobutylacetophenone 98%
7	p-Hydroxyacetophenone 96%
6	p-Methoxyacetophenone 97%
9	p-Phenoxyacetophenone 98%

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A continuous process for producing an acetyl-substituted aromatic compound using an anhydrous hydrogen fluoride catalyst which comprises
obtaining an acetyl fluoride by the reaction of excess acetic anhydride with an anhydrous hydrogen fluoride wherein the ratio of excess acetic anhydride to hydrogen fluoride is 5 mol% or below, and separating formed acetyl fluoride by distillation,
reacting an aromatic compound selected from alkyl-benzenes, alkyl-naphthalenes, phenols, naphtholes or aromatic ethers with the separated acetyl fluoride in the presence of anhydrous hydrogen fluoride as a catalyst, and
thermally decomposing the resulting complex compound between the acetyl-substituted aromatic compound and hydrogen fluoride in the presence of a solvent which is inert to hydrogen fluoride.
2. The continuous process according to Claim 1, wherein the reaction pressure in acetylation is from atmospheric pressure to $2 \text{ kg/cm}^2\text{G}$.
3. The continuous process according to Claim 1, wherein the reaction temperature of acetylation is from 0 to 70°C .

DATED THIS 16TH DAY OF JANUARY, 1989
MITSUBISHI GAS CHEMICAL COMPANY, INC.

By Its Patent Attorneys:

GRIFFITH HACK & CO.

Fellows Institute of Patent
Attorneys of Australia



FIG. 1

