Oct. 4, 1949. J. A. SHAW ET AL 2,483,440

SILVER ACETYLIDE COMPOUND AND PROCESS OF MAKING SAME

Filed Feb. 7, 1946

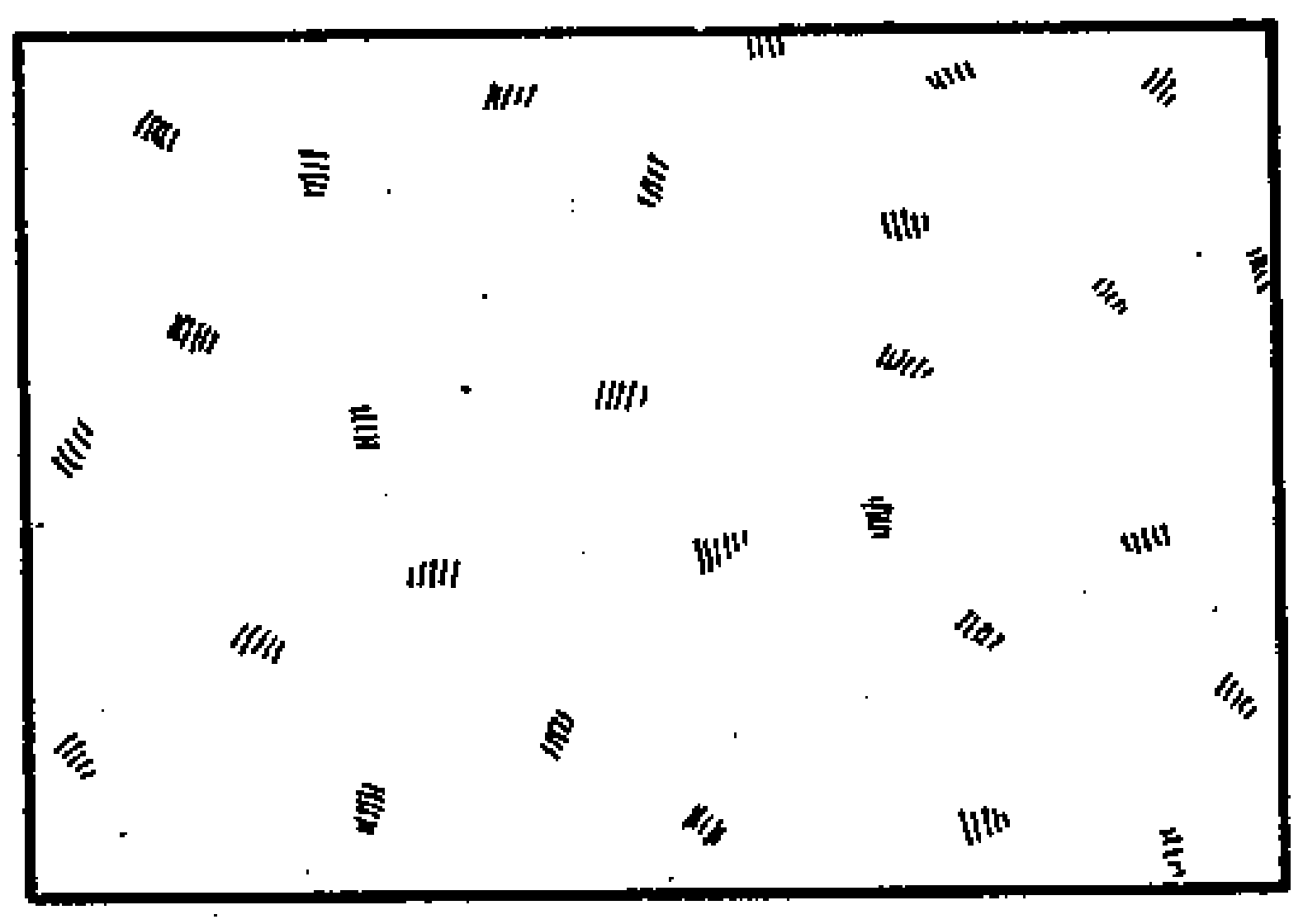

Fig: 1.

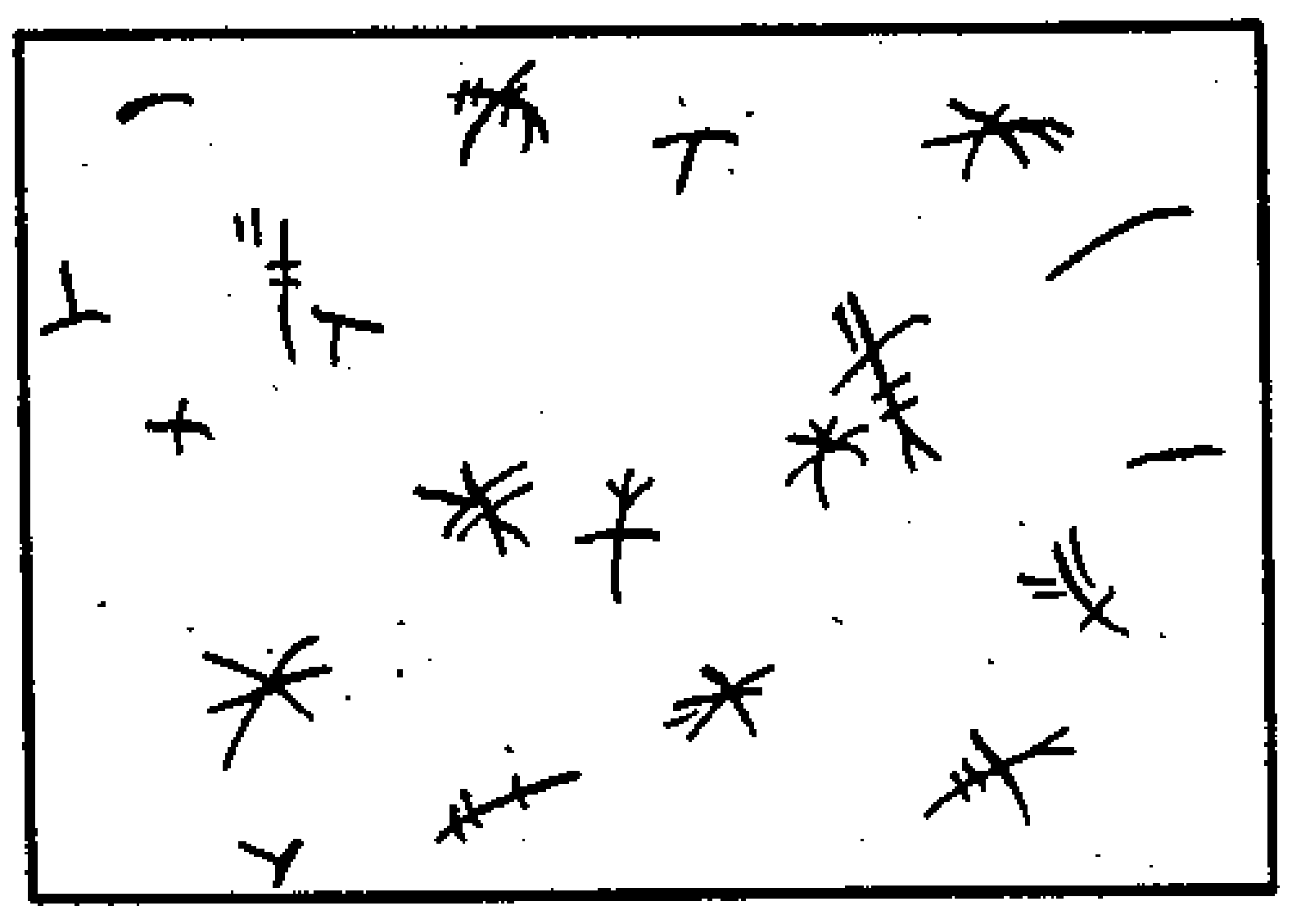

Fig: 2.

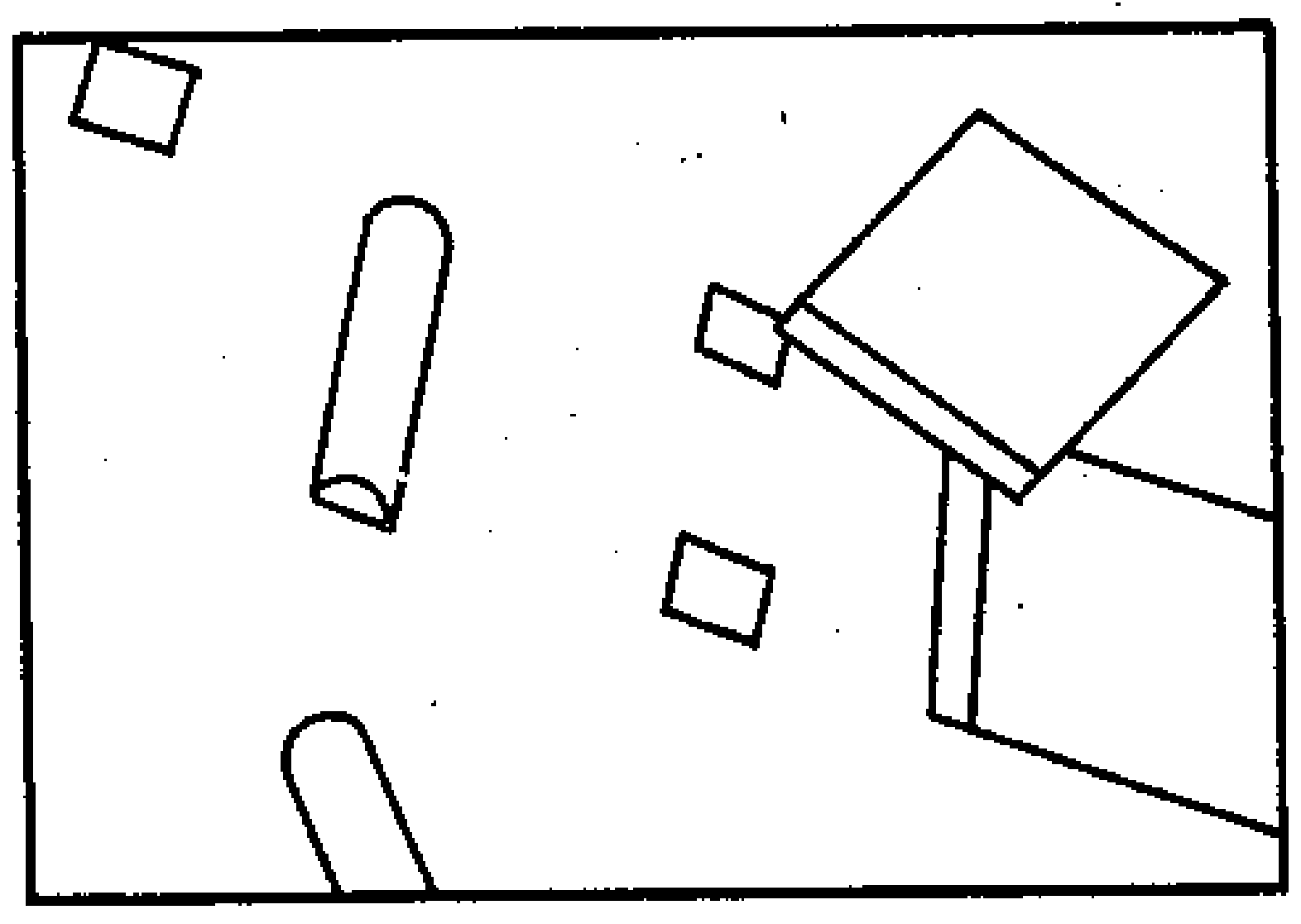

Fig: 3.

WITNESSES:
E. J. Maloney.
Phyllis Passero

INVENTORS.
ELTON FISHER, &
JOSEPH A. SHAW.
BY Edmund J. Borden
their ATTORNEY

Patented Oct. 4, 1949 **2,483,440**

UNITED STATES PATENT OFFICE

2,483,440

SILVER ACETYLIDE COMPOUND AND PROCESS OF MAKING SAME

Joseph A. Shaw and Elton Fisher, Pittsburgh, Pa., assignors to Koppers Company, Inc., Pittsburgh, Pa., a corporation of Delaware

Application February 7, 1946, Serial No. 646,185

2 Claims. (Cl. 260—430)

This invention relates to a silver acetylide compound. More particularly the invention relates to a non-explosive silver acetylide compound and the process of making the compound.

It is well known that silver nitrate is an effective absorbent for olefines. However, the use of silver nitrate has been avoided commercially for absorption of olefines, such as ethylene and propylene from coke oven or coal gas because such gases also contain acetylene. Acetylene customarily reacts with the silver nitrate to form silver acetylide $Ag_2C_2.AgNO_3$, which is a dangerous and powerful explosive. A rise in temperature to about 210° C. or an electrostatic spark are sufficient to detonate the dry substance.

Coke oven and coal gas contain hydrogen as well as olefines and acetylene. If silver nitrate solution of strong concentration is used for absorbing the olefines, the hydrogen reduces the silver nitrate to deposit metallic silver from the absorbent solution with the consequent loss of expensive silver nitrate and interference with smooth mechanical operation of the process. For this reason dilute silver nitrate has been used as an absorbent solution, which was accompanied by the inevitable explosion risk.

The present invention is based upon the discovery that a strong silver nitrate solution may be safely used for the absorption of olefines that are associated with acetylene. Such strong silver nitrate solutions react with the acetylene to form a new compound of silver and acetylene, which can be safely handled without explosion risk.

The primary object of the present invention is to provide a new compound, silver acetylide $Ag_2C_2.6AgNO_3$, and the method of making the compound.

With this and other objects in view, the invention consists in the new silver acetylide compound $Ag_2C_2.6AgNO_3$, and the process of making the acetylide.

The principal application of the present invention is described in the co-pending application of Joseph A. Shaw, Ser. No. 637,740, filed December 28, 1945, for "Treatment of coke oven gas," now abandoned.

To produce the new compound silver acetylide, $Ag_2C_2.6AgNO_3$, acetylene C_2H_2 is bubbled through a solution of silver nitrate having a concentration of more than 20% anhydrous $AgNO_3$ in the solution. From many tests it has been found that a silver nitrate solution containing 31% anhydrous silver nitrate ($AgNO_3$) gives a very desirable product. This strong silver nitrate solution will normally be reduced by hydrogen associated with acetylene gas, particularly if coke oven or coal gas is being used as the source of acetylene. It has been found that if a small amount of ferric nitrate $Fe(NO_3)_3$, is contained in the silver nitrate solution, metallic silver will not be precipitated.

If acetylene is bubbled through a weak solution of silver nitrate, that is 10% or less by weight of anhydrous $AgNO_3$ in the solution, a white crystalline compound $Ag_2C_2.AgNO_3$ is formed. This compound is very explosive under moderate heating and therefore involves risk in its formation and handling. The explosive silver acetylide is not very soluble in the dilute silver nitrate solution, but as the concentration of the silver nitrate solution is increased, the solubility of the explosive silver acetylide increases. As the strength of the silver acetylide solution used for absorption is increased up to 20% the explosive silver acetylide compound dissolves in the solution and tends to change its form from the explosive silver acetylide over to the safe silver acetylide compound $Ag_2C_2.6AgNO_3$.

In Table 1 is shown the solubility of the silver acetylide compound in the silver nitrate absorption solution and illustrates how the explosive silver acetylide is transformed into the safe silver acetylide compound.

TABLE 1

Solubility of silver acetylide in its mother liquor

Solubility Grams per Litre	Formula of Crystals	Type of Mother Liquor (Aqueous Solutions)	Temp. °C.
Trace	$Ag_2C_2AgNO_3$	0.1 N $AgNO_3$	25
0.532	do	10% $AgNO_3$ in N HNO_3	28
12.9	$Ag_2C_26AgNO_3$	20% $AgNO_3$ in N HNO_3	28
13.4	do	25% $AgNO_3$ in N HNO_3	28
19.9	do	35% $AgNO_3$ in N HNO_3	25
4.48	do	31% $AgNO_3$; 3.2% Fe $(NO_3)_3$; 11% HNO_3	25

With reference to Table 1 it may be stated that as the acetylene reacts with the silver nitrate solution, nitric acid is formed. Also nitric acid acts to minimize the precipitation of metallic silver by hydrogen. Commercially we are accordingly principally interested in acidified silver nitrate solutions. For this reason nitric acid was added to the solution in providing the data of Table 1. The presence of nitric acid in the solution tends to decrease the solubility of the silver acetylide compounds in the silver nitrate solution. However, the strength of the silver nitrate solution as it increases tends to compensate the reduction in solubility caused by the nitric acid. The mother liquor at the bottom of the table which consists of 31% silver nitrate solution, 3.2% of ferric nitrate solution, and 11% of nitric acid is the preferred adsorption solution which is used for absorbing acetylene and olefines from a gas containing hydrogen such as coke oven gas or coal gas. It will be seen that the solubility of the silver acetylide in this absorption solution is less than in the 20% or stronger silver nitrate solutions. With such an absorption solution, however, the silver nitrate will not be reduced to deposit metallic silver.

When the explosive silver acetylide compound is formed in very dilute silver nitrate solution, the substance, $AG_2C_2AgNO_3$, appears as minute needle-like crystals as illustrated in Figure 1. If the silver nitrate concentration of the acetylene treated solution be about 3–5%, much larger and longer needles and crosses appear and if the strength of the solution be still further increased, the small needles disappear leaving only the large needles and crosses as illustrated in Figure 2. Careful chemical analysis has shown, however, that both of these classes of crystals have the chemical formula $Ag_2C_2\text{-}AgNO_3$ and both are dangerous devastating explosives. If the concentration of the silver solution be sufficiently increased to 25% or above, these crystals will go into solution. If the volume be sufficient, the solution will be permanent. Apparently the only way to obtain the $Ag_2C_2AgNO_3$ complex from this solution is to redilute the solution or otherwise diminish the concentration of silver nitrate as by chemical means. If the volume is insufficient to maintain a clear solution, a silver acetylide complex will be precipitated, but the precipitate will be the rhombohedral crystals of $Ag_2C_26AgNO_3$, a substantially non-explosive material as illustrated in Figure 3.

Likewise, if acetylene or an inert gas containing acetylene be passed through a silver nitrate solution, a silver carbide precipitate will be formed. If the scrubbing solution has a low concentration of silver nitrate, only a small portion of the acetylene will be removed in any one scrubbing stage, as evidenced by the fact that many scrubbing stages may be placed in series and $Ag_2C_2AgNO_3$ will appear in the last stage long before the silver nitrate in the first stage has been seriously depleted. But where solutions of about 25% silver nitrate or higher concentration are employed, no initial precipitation of silver carbide takes place at all. However, our tests show that even with coke oven gas carrying only 0.05% acetylene and passing at the rate 0.5 cubic feet per hour through a half inch diameter test tube containing about a one inch seal of 30% silver nitrate, ninety-eight per cent of the acetylene is removed in the first pass. This is quite an unusual scrubbing efficiency and certainly is evidence of a chemical combination of the acetylene with the silver nitrate, even though no precipitate is formed.

Based on this characteristic of strong silver nitrate solutions, we were able to design a rather excellent analytical method for the direct determination of even traces of acetylene in gas by direct scrubbing of a gas stream with strong silver nitrate solution, followed by high dilution with water, filtering and weighing of the $Ag_2C_2AgNO_3$. Previously no such method was available.

When acetylene addition to the previously mentioned strong solution is carried sufficiently far, a silver carbide does precipitate out in accordance with fixed solubility laws. This precipitate is wholly the rhombohedral crystal of $Ag_2C_26AgNO_3$ shown in Figure 3 of the drawing. The

$$Ag_2C_26AgNO_3$$

has a pronounced tendency to form supersaturated solutions in strong silver nitrate solution. A clear supersaturated solution may be maintained for several weeks, but upon vigorous shaking a copious precipitation of $Ag_2C_26AgNO_3$ will precipitate.

In Table 2 is shown the form of crystalline silver acetylides formed with different strengths of silver nitrate solutions. As might be expected in borderline concentrations two of these crystal forms can exist simultaneously but these areas are rather narrow.

TABLE 2

Form of precipitate expectancy

[10 ml. $AgNO_3$ used at 25° C. in all instances]

Vol. ml. C_2H_2	Type of Solution	Results (Determined Microscopically)
1.8	15% $AgNO_3$ 1 N HNO_3	No precipitate.
3.0	do	Needles with crosses.
5.0	20% $AgNO_3$ 1 N HNO_3	No precipitate.
7.47	do	A few rhombs.
10.0	do	Rhombs and a few crosses.
15	do	Mostly crosses but a few rhombs.
24.9	25% $AgNO_3$ 1 N HNO_3	Rhombs only.

In the accompanying drawing are illustrated in Figures 1 and 2 photomicrographs of the silver acetylide compound $Ag_2C_2.AgNO_3$. The photomicrographs of Figures 1 and 2 are 120 diameters while the photomicrograph in Figure 3 is 70 diameters. The crystals of Figure 1 are precipitated from a one hundredth normal silver nitrate solution while the crystals of Figure 2 are precipitated from an 8% silver nitrate solution. It will be seen that the crystal structure of the $Ag_2C_2.AgNO_3$ is very fine needle-like crystals while the crystal structure of the acetylide

$$Ag_2C_2.6AgNO_3$$

is large rhombohedral crystals.

The silver acetylide $Ag_2C_2.6AgNO_3$ has been referred to as a safe acetylide compound. This compound will decompose when heated to a moderate temperature but the decomposition is not a violent explosive decomposition such as the explosion or decomposition of the compound $Ag_2C_2.AgNO_3$ when heated to its detonative temperature. The compound $Ag_2C_2.6AgNO_3$ is in the form of comparatively large white rhombohedral crystals which, in polarized light, exhibit a high degree of coloration, but are water-white in transmitted light. If the rhombohedral crystals or a strong silver nitrate solution containing the rhombohedral crystals is diluted with water, the rhombohedral crystals will be decomposed and form the explosive type of silver acetylide crystals.

The rhombohedral crystals may be separated from the solution in which they are precipitated by decantation or filtration. However, the silver nitrate solution always contains some silver acetylide in solution. In order to separate all of the silver acetylide from the silver nitrate solution, the acetylide compound may be precipitated by mercuric nitrate to form a mercury acetylide silver nitrate compound $HgC_2.3AgNO_3$, which may then be separated from the silver nitrate solution by decantation or filtration or the acetylene may be destroyed by boiling the above mercury precipitate with an excess of mercuric nitrate and nitric acid.

X-ray diffraction analyses were made of the $Ag_2C_2.AgNO_3$ and $Ag_2C_2.6AgNO_3$. The lines on the stable salt $Ag_2C_2.6AgNO_3$ diffraction analyses were quite clear and distinct and could be taken with a comparatively short exposure. On the other hand, the lines on the X-ray diffraction analyses of the explosive compound $Ag_2C_2.AgNO_3$ were very faint and, in fact, a very long exposure of the camera was required to get any picture. The heat energy of the X-ray camera apparently acted to decompose the salt while the exposure was being taken. Many attempts were made to get a good exposure but it would appear that the salt would decompose before an analysis showing the lines could be made.

The preferred form of the invention having been thus described, what is claimed as new is:

We claim:

1. A silver acetylide $Ag_2C_2.6AgNO_3$ crystallizable as white rhombohedral crystals, which are readily soluble in strong silver nitrate solutions.

2. A process of making silver acetylide $Ag_2C_2.6AgNO_3$ comprising: absorbing acetylene in an aqueous solution of silver nitrate containing nitric acid in which the concentration of silver nitrate during absorption is maintained at greater than 20% by weight of the solution.

JOSEPH A. SHAW.
ELTON FISHER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,875,924	Horsley	Sept. 6, 1932
2,150,349	Van Peski et al.	Mar. 14, 1939

OTHER REFERENCES

Stettbacher I, Zentralblatt Chem. II, 1919, pages 126 and 127.

Stettbacher II, Chem. Abstracts, vol. 35 (1941), page 3091.

Chavastelon, Compte rendu, vol. 124, pages 1364 and 1365 (1897).

(Copies in Patent Office Library.)