

# UNITED STATES PATENT OFFICE

2,256,759

## AMIDINE SALTS OF AMINOBENZOIC ACIDS

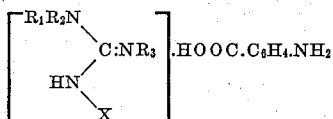
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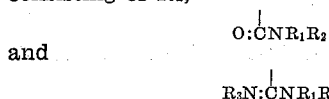
15 Claims. (Cl. 260—501)

This invention relates to amidine salts of aminobenzoic acids such as anthranilic acid and meta- and para-aminobenzoic acids and to methods of preparing the same. I have found that certain well-defined amidine salts of these aminobenzoic acids can be formed, which salts have unusual properties of considerable commercial importance. They exert a remarkable stabilizing action on photographic developing solutions when incorporated therein.

The amidines which I have found to form salts with aminobenzoic acids may be defined as amino-amidines; that is to say, amidines in which the alkyl or aryl group has been replaced by an amino or substituted amino group. The compounds may therefore be represented by the type formula



in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals and X is a member of the group consisting of R<sub>1</sub>,



The substituents R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> may be the same or different in various compounds included within the scope of the invention and it should be understood that each symbol is intended to represent any member of the group defined.

The amidine salts represented by the above type formula are true addition products; that is to say, the carboxylic acid group adds on to the organic base to form a salt. I believe that this addition takes place at one of the nitrogen atoms of the amidine, which undergoes a change of valence of from 3 to 5, but this fact has not as yet been definitely established for any of the salts of organic nitrogen bases. Accordingly, the above formula represents the customary method of designating addition products of this nature, this method consisting simply in showing the formula of the base in juxtaposition to the formula of the acid.

An inspection of the above type formula will show that the amidine salts of my invention are salts of guanidine and its derivatives and substitution products, and particularly guanidine itself, guanylurea, biguanide, and their alkyl, hy-

droxyalkyl and aryl substitution products. These compounds are all organic bases, and are sufficiently basic to enable them to form salts with aminobenzoic acids such as anthranilic acid.

Any guanidine base may be used for this purpose, such as guanidine itself, dimethyl or trimethyl guanidine, dibutyl guanidine, mono-, di- or triphenyl guanidine, ditolyl guanidine, or alkoxy substituted guanidines such as mono-, di- or triethanol guanidine and the like. Similarly, such guanylurea compounds as guanylurea itself, mono- or dimethyl guanylurea, diphenyl guanylurea, tetraethyl guanylurea, and triethanol guanylurea are organic bases which will form salts of anthranilic acid and meta- and para-aminobenzoic acids.

Biguanide and such substituted biguanides as mono- and dimethyl and diethyl biguanides, diamyl biguanide, 1,5 diallyl biguanide, 1,1,5,5 tetramethyl biguanide, 1,1,2 trimethyl biguanide and 1,2,3 triphenyl biguanide will also form salts of aminobenzoic acids in accordance with the invention. It should be noted however that the biguanides, as well as the other amidine bases included in the invention, will form both neutral and acid salts with dibasic mineral acids such as sulfuric acid. These two classes of salts will, in turn, form salts containing one and two molecular equivalents of anthranilic acid for each mole of the biguanide or other amidine compound respectively. It should be understood that both classes of salts are included in the invention.

Many of the salts of my invention may be prepared by simply mixing a solution containing the free amidine base or its carbonate with a solution of aminobenzoic acid such as an anthranilic acid solution. In many cases it is convenient to start with the amidine sulfate, hydrochloride or other mineral acid salt, from which the free base can be liberated by dissolving in alcohol, addition of an alkali such as sodium hydroxide, and removal of the precipitated sodium sulfate, sodium chloride or other salt.

The invention will be illustrated in greater detail by the following specific examples. It should be understood however that although these examples describe certain compounds constituting specific embodiments of the invention they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

### Example 1

164 parts of 98.2% guanidine carbonate are dissolved in 125 parts of warm water and the

solution filtered. Approximately 250 parts of C. P. anthranilic acid are added slowly with agitation. The mixture is then cooled to about 25° C. and filtered.

The residue is dissolved in 125 parts of hot water, cooled to about 25° C. and the crystals are filtered off and dried at room temperature. The product is guanidine anthranilate, a light-grey crystalline salt consisting of stout bevelled prisms of parallel extinction. The index of refraction parallel to length is about 1.514; across the length it is about 1.648. On long and continued exposure to light the crystals become slightly yellow.

The molecular weight of the new salt is 214. It melts at 65-66° C., and is soluble in water to the extent of 133 g. per 100 g. of water at 25° C. A 1 g. solution in 100 cc. of water exhibits a pH at 25° C. of 5.93 and a potential of +0.07 volt. Its analysis is shown in the following table:

Component	Percentage	
	Theor.	Det.
Nitrogen (N).....	26.20	26.36
Carbon (C).....	44.85	44.90
Hydrogen (H).....	6.54	6.50

From the analysis and molecular weight it is evident that the empirical formula of the compound is  $CN_3H_5.HOOC.C_6H_4.NH_2.H_2O$ .

Upon substituting for the guanidine equivalent quantities of substituted guanidines such as mono- or diphenyl guanidine, dimethyl, diethyl or mono-, di- or triethanol guanidine the corresponding substituted guanidine salts are obtained. These compounds are in general less soluble in water than is the extremely soluble guanidine anthranilate, but they are more soluble in organic solvents such as ethanol, solvent naphtha and the like. The diphenyl and dixyl guanidine anthranilates were found to be effective as mothproofing agents when prepared as a 4% solution in solvent naphtha.

#### Example 2

86.8 parts by weight of biguanide sulfate were dispersed in 400 parts by volume of ethyl alcohol, 32 parts by weight of sodium hydroxide were added and the mixture stirred for about 6 hours to insure complete reaction. The precipitate of sodium sulfate was then filtered off, leaving a solution of free biguanide in alcohol. To this solution there was added with stirring 54.8 parts of C. P. anthranilic acid, whereupon heat was generated and a clear solution was obtained. Upon standing, crystals of biguanide anthranilate separated out. The mixture was then stirred, filtered, and the crystals were washed with ethyl alcohol and dried under a vacuum.

Biguanide anthranilate is a white crystalline salt consisting of thin plates; sometimes octagonal but usually elongated and of parallel extinction. The index of refraction parallel to length is about 1.626; across the length it is about 1.723. Upon long and continued exposure to light the crystals become slightly pinkish in color. The salt melts at 187-188° C. and is soluble to the extent of 53 g. per 100 g. of water at 25° C. A solution of 1 g. in 100 g. of water exhibits at 25° C. a pH of 7.55 and a potential of +0.02 volt. The molecular weight of the salt is 238 which indi-

cates that the crystals are anhydrous. Its analysis is shown in the following table:

Component	Percentage	
	Theor.	Det.
Nitrogen (N).....	35.29	35.08
Carbon (C).....	45.40	45.62
Hydrogen (H).....	5.84	5.74

#### Example 3

145.2 parts by weight of guanylurea sulfate were dispersed in 400 parts by volume of ethyl alcohol, 16 parts by weight of sodium hydroxide were added and the mixture stirred for four hours to insure complete reaction of the guanylurea sulfate. The precipitate of sodium sulfate was then filtered off.

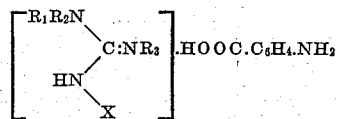
54.8 parts by weight of C. P. anthranilic acid were added to the filtrate with continuous agitation. The mixture was then stirred for one hour, the solids filtered off and washed with ethyl alcohol, and the resulting crystals dried in vacuo for about ten hours.

Guanylurea anthranilate is a white crystalline salt consisting of long slender prisms of parallel extinction. The index of refraction parallel to the length is about 1.535; across the length it is about 1.697. The crystals become slightly yellow upon long and continued exposure to light. They melt at 159-160° C. and are soluble in water to the extent of 2.3 g. per 100 cc. at 25° C. A 1% solution in water exhibits at 25° C. a pH of 6.43 and a potential of +0.07 volt. The molecular weight is 239, which indicates that the crystals are anhydrous. The analysis of the product is shown in the following table:

Component	Percentage	
	Theor.	Det.
Nitrogen (N).....	29.29	29.18
Carbon (C).....	45.20	45.14
Hydrogen (H).....	5.44	5.33

What I claim is:

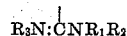
1. Salts of aminobenzoic acids of the formula



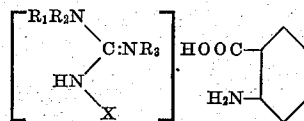
in which  $R_1$ ,  $R_2$  and  $R_3$  are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals and  $X$  is a member of the group consisting of  $R_1$ ,



and



2. Salts of aminobenzoic acids of the formula

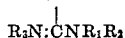


in which  $R_1$ ,  $R_2$  and  $R_3$  are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and

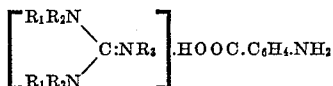
aryl radicals and X is a member of the group consisting of R<sub>1</sub>,



and

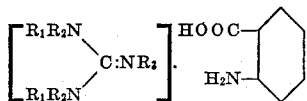


3. Salts of aminobenzoic acids of the formula



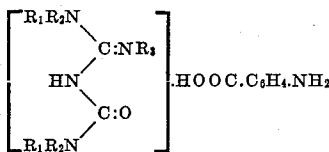
in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

4. Salts of aminobenzoic acids of the formula



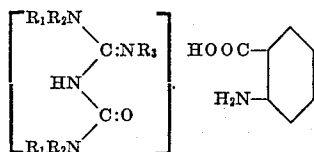
in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

5. Salts of aminobenzoic acids of the formula



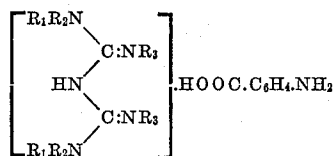
in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

6. Salts of aminobenzoic acids of the formula



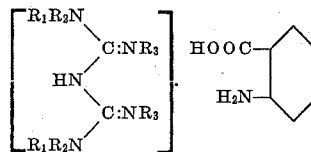
in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

7. Salts of aminobenzoic acids of the formula



in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

8. Salts of aminobenzoic acids of the formula



in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals.

9. A guanidine salt of an aminobenzoic acid.

10. A guanylurea salt of an aminobenzoic acid.

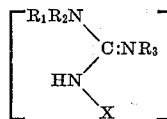
11. A biguanide salt of an aminobenzoic acid.

12. Guanidine anthranilate.

13. Guanylurea anthranilate.

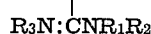
14. Biguanide anthranilate.

15. A method of preparing amidine salts of aminobenzoic acids which comprises mixing a solution of an amidine of the formula



in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are members of the group consisting of hydrogen, alkyl, hydroxyalkyl and aryl radicals and X is a member of the group consisting of R<sub>1</sub>,

and



with a solution of an aminobenzoic acid and separating the resulting compound from the solvent.

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