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2,061,632

SAFETY PAPER AND THE LIKE

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38 Claims. (Cl. 91—67.95)

This invention relates to safety paper and more particularly to paper and the like treated with a chemical or chemicals to render it sensitive to ink eradicating chemicals.

In the preparation of so-called safety papers a chemical compound is incorporated in the paper, which compound, upon the application of common ink eradicators to the paper, is decomposed or chemically altered, producing a conspicuous stain or discoloration upon the paper due to a change in the color of the chemical compound, thereby indicating that an attempt has been made to alter the original writing on the paper. Paper and the like of this type is particularly valuable for use in the preparation of bank checks, deeds, wills, drafts, stocks, and bonds, and other instruments representing values or records, and offers a protection against fraud.

Safety papers and chemicals employed in their preparation, which have been used up to the present time, have proven to be more or less unsatisfactory for the reason that the color which was developed with ink eradicators has not been striking or permanent and was easily removed with common chemicals, such as reducing agents. Furthermore, some of the prior safety papers are not fast to light, whereupon the paper becomes discolored when exposed to sunlight. Also, some of them lose their stain producing properties after exposure to sunlight or ageing for a short time.

An object of the present invention is to produce a safety paper which yields a conspicuous stain when treated with common ink eradicators which are used in removing writing or ink from the paper. A further object is to provide a paper of such type in which the stain produced by ink eradicators is of such permanent character that it is not removed by any chemical treatment which will leave the paper itself unaltered. A further object is to treat paper and the like with a chemical compound which is stable toward the action of light and air and atmospheric conditions of high humidity and elevated temperatures, whereby a material is produced which will not be discolored upon exposure to sunlight and varying atmospheric conditions and which will remain sensitive to ink eradicators for indefinite periods of time, even upon exposure to sunlight and varying atmospheric conditions. Other and further objects are to provide new compositions of matter and to advance the art. Other objects will appear hereinafter.

These objects may be accomplished according to my invention which comprises incorporating in paper and the like, a member of the class of organic compounds known as the amino-aryl-thiazoles and their derivatives and salts. The amino-aryl-thiazoles together with their derivatives and salts have been found to be especially suited to the preparation of safety paper. These compounds react with strong oxidizing agents such, for example, as hypochlorite, to yield highly colored, insoluble, and often very stable compounds. These oxidation products, especially when formed in or on paper or the like, by application of a bleach solution to the paper and the like, in which has been incorporated a thiazole, give a conspicuous color ranging from a yellow-brown to a purple, which color cannot be removed by further bleaching or oxidation or by the application of acids or alkalies, or by washing until the paper itself is destroyed.

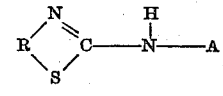
The term "amino-aryl-thiazoles" as employed throughout this specification and the claims is to be understood to include the various derivatives and their salts.

The amino-aryl-thiazoles, when pure, are colorless solids and are very fast to light, including direct sunlight, even when incorporated in paper. They are stable compounds and do not decompose on standing under atmospheric conditions, over long periods of time.

Since the amino-aryl-thiazoles are colorless when pure, they can be readily incorporated in white paper or paper of any color without altering the color or the shade until the paper is treated with an ink eradicator or an oxidizing agent to develop a characteristic stain.

When paper containing these compounds is treated with hypochlorite or other common ink eradicator, the stain produced develops rapidly and is formed under acid or alkaline conditions even in the presence of reducing agents, whenever the ink eradicator is applied in amounts sufficient to remove ordinary ink marks from the paper.

This class of compounds, the amino-aryl-thiazoles, may be employed as free bases or as salts, that is, as the hydrochloride, hydrobromide, hydroiodide, hydrofluoride, sulfate, phosphate, formate, acetate, or oxalate. These compounds, as the base or as the salt, may be employed in either aqueous solution or non-aqueous solution as in methyl or ethyl alcohols the alcohols being either pure or containing water. The amino-aryl-thiazoles forming the subject matter of my invention may be represented by the formula:

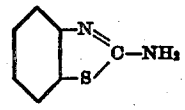


in which R represents an aryl nucleus having adjacent carbon atoms joined to the nitrogen and sulfur atoms respectively, and which may be unsubstituted or may contain one or more substituents and in which A represents hydrogen or an alkyl, aryl, or aralkyl group. When A represents an aryl or aralkyl radical the aryl nucleus

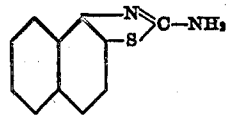
may be unsubstituted or may contain substituents. Some of the substituents which the aryl nuclei may contain are alkyl, alkoxy, halogen, amino, nitro, and sulfonic groups. Sulfonated amino-aryl-thiazoles have been found to be effective materials for safety paper, the sulfonated bases being more soluble and faster to light than the unsulfonated compounds.

Also, in general, the unsubstituted amino compounds, in other words, those in which A represents hydrogen are to be preferred because of their greater solubility and fastness to light. Among the compounds which I have found to be particularly satisfactory for my purpose are:

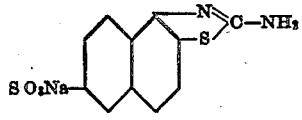
Amino-benzo-thiazole



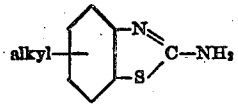
Amino-a-naphtho-thiazole



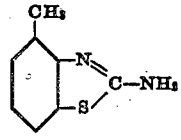
1-amino-5-sulfonic-a-naphtho-thiazole



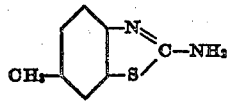
Amino alkyl benzo-thiazoles



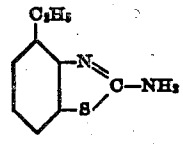
1-amino-3-methyl-benzo-thiazole



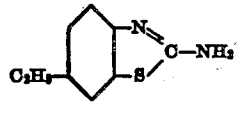
1-amino-5-methyl-benzo-thiazole



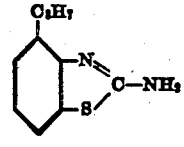
1-amino-3-ethyl-benzo-thiazole



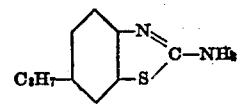
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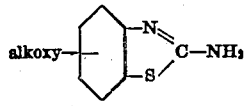
1-amino-3-propyl-benzo-thiazole



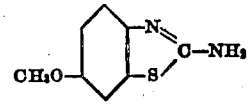
1-amino-5-propyl-benzo-thiazole



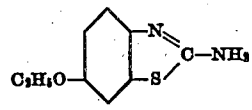
Amino-alkoxy-benzo-thiazoles



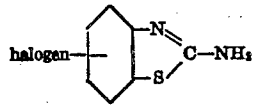
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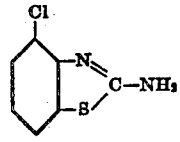
1-amino-5-ethoxy-benzo-thiazole



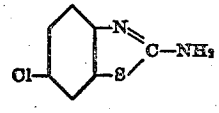
Amino-halogen-benzo-thiazoles



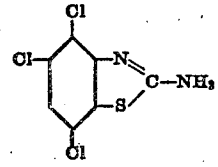
1-amino-3-chloro-benzo-thiazole



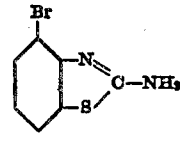
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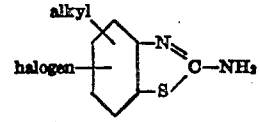
1-amino-3, 4, 6-trichloro-benzo-thiazole



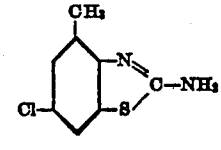
1-amino-3-bromo-benzo-thiazole



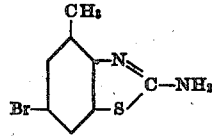
Amino-alkyl-halogen-benzo-thiazoles



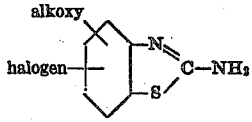
1-amino-3-methyl-5-chloro-benzo-thiazole



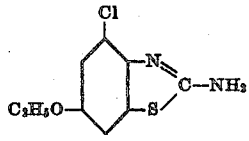
1-amino-3-methyl-5-bromo-benzo-thiazole



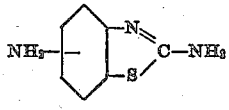
Amino-alkoxy-halogen-benzo-thiazoles



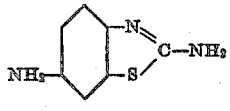
1-amino-5-ethoxy-3-chloro-benzo-thiazole



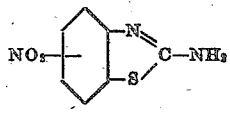
Amino-amino-benzo-thiazoles



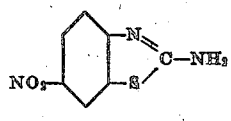
1:5-amino-benzo-thiazole



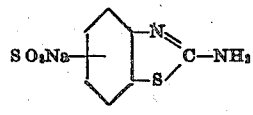
Amino-nitro-benzo-thiazoles



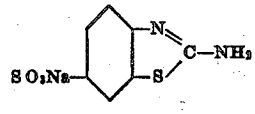
1-amino-5-nitro-benzo-thiazole



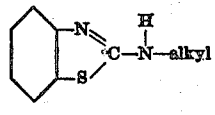
Amino-sulfonic benzo-thiazoles



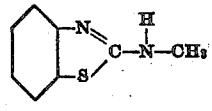
1-amino-5-sulfonic-benzo-thiazole



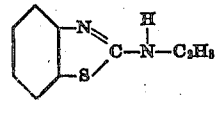
1-(alkyl)-amino-aryl-thiazoles



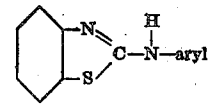
1-(methyl)-amino-benzo-thiazole



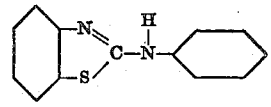
1-(ethyl)-amino-benzo-thiazole



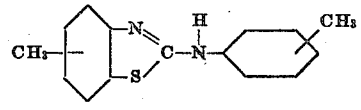
1-(aryl)-amino-aryl-thiazoles



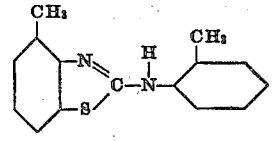
1-(phenyl)-amino-benzo-thiazole



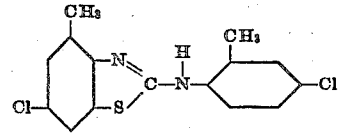
1-(tolyl)-tolidinyl-thiazoles



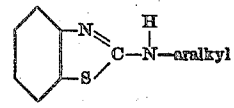
1-(2-methyl-phenyl)-amino-3-methyl-benzo-thiazole



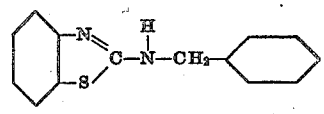
1-(4-chloro-2-methyl-phenyl)-amino-3-methyl-5-chloro-benzo-thiazole



1-(aralkyl)-amino-aryl-thiazoles



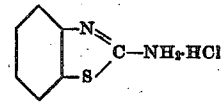
1-(benzyl)-amino-benzo-thiazole



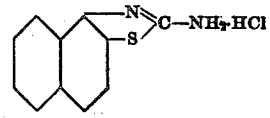
The salts of any of the above compounds or their analogues have proved to be particularly effective. Illustrative examples of some of these salts follow:

Hydrochlorides

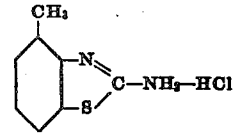
1-amino-benzo-thiazole hydrochloride



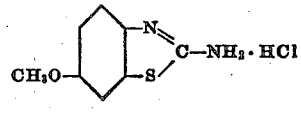
1-amino-a-naphtho-thiazole hydrochloride



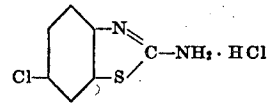
1-amino-3-methyl-benzo-thiazole hydrochloride



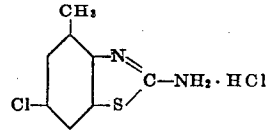
1-amino-5-methoxy-benzo-thiazole hydrochloride



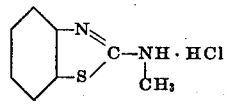
1-amino-5-chloro-benzo-thiazole hydrochloride



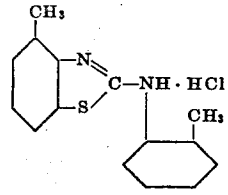
1-amino-3-methyl-5-chloro-benzo-thiazole hydrochloride



1-(methyl)-amino-benzo-thiazole hydrochloride

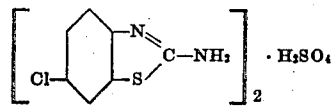


1-(2-methyl-phenyl)-amino-3-methyl-benzo-thiazole hydrochloride

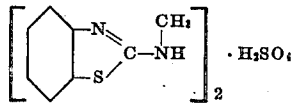


Sulfates

1-amino-5-chloro-benzo-thiazole sulfate

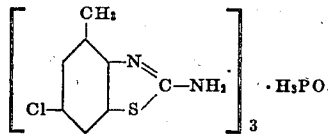


1-(methyl)-amino-benzo-thiazole sulfate

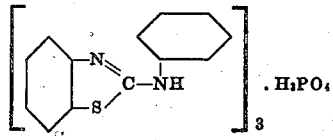


Phosphates

1-amino-3-methyl-5-chloro-benzo-thiazole phosphate

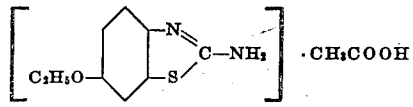


1-(phenyl)-amino-benzo-thiazole phosphate

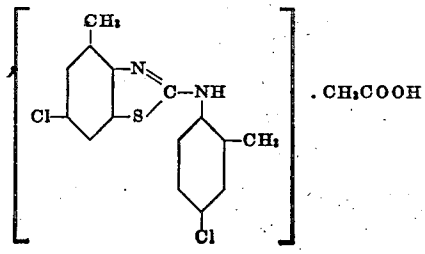


Acetates

1-amino-5-ethoxy-benzo-thiazole acetate



1-(4-chloro-2-methyl-phenyl)-amino-3-methyl-5-chloro-benzo-thiazole acetate



Other compounds which have been found to be effective for my purpose are sulfonated 1-amino-3-methyl-benzo-thiazole, sulfonated 1-amino-5-ethoxy-benzo-thiazole and their salts. Many other compounds falling within the class will readily occur to those skilled in the art and my invention is intended to include all such compounds.

The application of amino-aryl-thiazoles, their derivatives and salts, to paper will be a simple matter to those skilled in the manufacture of paper. These substances may be incorporated in the pulp itself, that is, by adding them to the beater. Further, they can be added to the paper, in solution or in suspension, with the sizing. They can also be applied to the surface of the paper by dipping or calendering operations. The salts of the amino-aryl-thiazoles, for example, the hydrochlorides, appear to have an affinity for the cellulose fiber since they are exhausted from the suspension of pulp in the beater, and the thiazoles can be efficiently applied in this manner. The hydrochlorides may also be applied in any of the ways above mentioned. Since these compounds can be applied to paper in any one of a number of routine operations employed in the manufacture of paper, it will be evident that this method of producing safety paper can be carried out at a minimal cost. The amount of amino-aryl-thiazole employed will vary with the intensity of the stain desired. However, it has been found that when the amino-aryl-thiazole is added to the pulp in the beater, 1–5 pounds of the thiazole per thousand pounds of pulp will give a finished paper which will yield a deep indelible stain. Smaller or larger amounts may be employed, if desired. However, the above proportions have been found to be satisfactory for most purposes. Similar proportions may be employed when the substances are incorporated in the paper in the other ways above mentioned, although smaller quantities will generally be employed.

Other materials, such as parchment, textiles, wood fibre, wood, and in fact any material upon which it may be desired to write or print letters or designs with ink and obtain protection against alteration of the writing or predetermined design, may be treated with the compounds of my invention. Accordingly, when I refer to "paper and the like" in the specification and claims, I intend to include, thereby, all such materials.

While I have described certain specific compounds of a class, and methods of preparing safety paper therewith, it will be obvious to those skilled in the art that there are many other compounds falling within the class which may be employed and other methods for incorporating the same into paper may also be employed, without departing from the spirit of my invention. Accordingly, the scope of my invention is to be limited solely by the appended claims construed as broadly as is permissible in view of the prior art.

I claim:

1. Paper and the like having incorporated therein a 1-amino-5-chloro-benzo-thiazole.

2. Paper and the like having incorporated therein 1-amino-5-chloro-benzo-thiazole hydrochloride.

3. Paper and the like having incorporated therein a 1-amino-alpha-naphtho-thiazole.

4. Paper and the like having incorporated therein 1-amino-alpha-naphtho-thiazole hydrochloride.

5. Paper and the like having incorporated

therein a 1-amino-3-methyl-5-chloro-benzothiazole.

6. Paper and the like having incorporated therein 1-amino-3-methyl-5-chloro-benzo-thiazole hydrochloride.

7. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole compound containing the 1-amino-arylthiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

8. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole compound containing the 1-amino-arylthiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens.

9. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-aryl-thiazole compound containing the 1-amino-arylthiazole nucleus in which the amio nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen and the aryl group contains at the most two benzene rings.

10. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole compound containing the 1-amino-arylthiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings.

11. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole compound containing the 1-amino-arylthiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen and the aryl group contains at the most two benzene rings and has at least one substituent selected from the group consisting of alkyl, alkoxy, halogen, amino, nitro and sulfonic groups.

12. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole compound containing the 1-amino-arylthiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings and has at least one substituent selected from the group consisting of alkyl, alkoxy, halogen, amino, nitro and sulfonic groups.

13. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole compound containing the 1-amino-arylthiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has one free amino hydrogen and one amino hydrogen replaced by a carbon atom of an organic group.

14. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole compound containing the 1-amino-arylthiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has one free amino hydrogen and one amino hydrogen replaced by a carbon atom of an organic hydrocarbon radical.

15. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

16. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens.

17. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen and the aryl group contains at the most two benzene rings.

18. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings.

19. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings and has at least one substituent selected from the group consisting of alkyl, alkoxy, halogen, amino, nitro and sufonic groups.

20. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a 1-amino-arylthiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has one free amino hydrogen and one amino hydrogen replaced by a carbon atom of an organic hydrocarbon radical.

21. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a salt comprising the combination of an acid with a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

22. The method of rendering paper and the like sensitive to ink eradicating chemicals which comprises incorporating therein a salt comprising the combination of a non-oxidizing acid with a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

23. Paper and the like having incorporated therein a 1-amino-aryl-thiazole compound containing the 1-amino-aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

24. Paper and the like having incorporated therein a 1-amino-aryl-thiazole compound containing the 1-amino-aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens.

25. Paper and the like having incorporated

therein a 1-amino-aryl-thiazole compound containing the 1-amino-aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen and the aryl group contains at the most two benzene rings.

26. Paper and the like having incorporated therein a 1-amino-aryl-thiazole compound containing the 1-amino-aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings.

27. Paper and the like having incorporated therein a 1-amino-aryl-thiazole compound containing the 1-amino-aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen and the aryl group contains at the most two benzene rings and has at least one substituent selected from the group consisting of alkyl, alkoxy, halogen, amino, nitro and sulfonic groups.

28. Paper and the like having incorporated therein a 1-amino-aryl-thiazole compound containing the 1-amino-aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings and has at least one substituent selected from the group consisting of alkyl, alkoxy, halogen, amino, nitro and sulfonic groups.

29. Paper and the like having incorporated therein a 1-amino-aryl-thiazole compound containing the 1-amino-aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has one free amino hydrogen and one amino hydrogen replaced by a carbon atom of an organic group.

30. Paper and the like having incorporated therein a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

31. Paper and the like having incorporated therein a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens.

32. Paper and the like having incorporated therein a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen and the aryl group contains at the most two benzene rings.

33. Paper and the like having incorporated therein a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings.

34. Paper and the like having incorporated therein a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has two free amino hydrogens and the aryl group contains at the most two benzene rings and has at least one substituent selected from the group consisting of alkyl, alkoxy, halogen, amino, nitro and sulfonic groups.

35. Paper and the like having incorporated therein a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has one free amino hydrogen and one amino hydrogen replaced by a carbon atom of an organic hydrocarbon radical.

36. Paper and the like having incorporated therein a salt comprising the combination of an acid with a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

37. Paper and the like having incorporated therein a salt comprising the combination of a non-oxidizing acid with a 1-amino-aryl-thiazole in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

38. Bank checks having incorporated therein a 1-amino-aryl-thiazole compound containing the 1-amino aryl-thiazole nucleus in which the amino nitrogen is directly bonded to the carbon of the thiazole ring and has at least one free amino hydrogen.

SAMUEL LENHER.