SUMMARY

The invention is based, in part, on the discovery that by irradiating paper at appropriate levels, the functionalization of the irradiated paper can be altered, thereby making the paper distinguishable, e.g., by infrared spectrometry (IR) or other techniques, from paper that has not been irradiated. In some cases, the paper is also distinguishable from paper that has been irradiated, but under other process conditions. As a result, paper products such as currency can be "marked" by the methods described herein. In some implementations, the marking is invisible to the naked eye, e.g., it is detected by the use of instruments. In other implementations, the marking is visible to the naked eye. Generally, the marking is difficult to replicate without relatively sophisticated equipment, thereby making counterfeiting more difficult.

By "functionalization," we mean the functional groups that are present on or within the paper.

~~In one aspect, t~~The ~~invention~~ disclosure features methods of making a marked paper product. Some methods include irradiating a paper product under conditions selected to alter the functionalization of at least an area of the paper product. One aspect relates to a method comprising: marking unmarked paper or paper products by irradiation, wherein irradiation comprises exposure to accelerated electrons and/or accelerated particles heavier than an electron and wherein the paper or paper product is irradiated with a total dosage of at least 0.1 Mrad and the electrons or particles have an energy of at least 0.25 MeV.

Some implementations include one or more of the following features. The paper can be irradiated with ionizing radiation. The dose of ionizing radiation can be at least, for example, 0.10 MRad, e.g., at least 0.25 MRad. The dose of ionizing radiation can be controlled to a level of about 0.25 to about 5 MRad. Irradiating can include irradiating with gamma radiation, and/or with electron beam radiation or other particles. Electrons in the electron beam can have an energy of at least 0.25 MeV, e.g., from about 0.25 MeV to about 7.5 MeV.

The methods can further include quenching the irradiated paper product. For example, quenching can be performed in the presence of a gas selected to react with radicals present in the irradiated paper product.

In some cases, only a portion of the paper product is irradiated. In some cases, only a portion of the irradiated area, or only a portion of the paper product as a whole, is quenched. For example, an area that is to remain unmarked and/or unquenched can be masked.

WHAT IS CLAIMED IS:

1. A method of making a marked paper product, the method comprising irradiating a paper product under conditions selected to alter the functionalization of at least an area of the paper product.

2. The method of claim 1 wherein the paper is irradiated with ionizing radiation.

3. The method of claim 1 wherein the dose of ionizing radiation is at least 0.10 MRad.

4. The method of claim 1 wherein the dose of ionizing radiation is at least 0.25 MRad.

5. The method of claim 1 wherein irradiating comprises irradiating with ganima radiation, and/or with electron beam radiation.

6. The method of claim 5 wherein the electron beam has an energy of at least 0.25 MeV.

7. The method of claim 1 wherein irradiating is performed under conditions selected to increase the number of carboxylic acid groups present in the paper product.

8. The method of claim 1 further comprising quenching the treated paper product.

9. The method of claim 8 wherein quenching is performed in the presence of a gas selected to react with radicals present in the irradiated paper product.

10. The method of claim 1 wherein only a portion of the paper product is irradiated.

11. The method of claim 8 wherein only a portion of the paper product is quenched.

12. A marked paper product comprising a cellulosic or lignocellulosic fibrous material containing functional groups not present in a naturally occurring cellulosic or lignocellulosic fibrous material from which the paper product was obtained.

13. The marked paper product wherein the cellulosic or lignocellulosic fibrous material in the marked paper contains a greater number of carboxylic acid groups than are present in the naturally occurring cellulosic or lignocellulosic fibrous material.

14. The marked paper product of claim 12 wherein the cellulosic or lignocellulosic fibrous material in the marked paper includes functional groups selected from the group consisting of aldehyde groups, nitroso groups, nitrile groups, nitro groups, ketone groups, amino groups, alkyl amino groups, alkyl groups, chloroalkyl groups, chlorofluoroalkyl groups, and enol groups.

15. The marked paper product of claim 12 wherein the cellulosic or lignocellulosic fibrous material in the marked paper includes a plurality of saccharide units arranged in a molecular chain, and from about 1 out of every 5 to about 1 out of every 1500 saccharide units comprises a nitroso, nitro, or nitrile group.

16. The marked paper product of claim 12 wherein the cellulosic or lignocellulosic fibrous material in the marked paper comprises a mixture of nitrile groups and carboxylic acid groups.

17. The marked paper product of claim 15 wherein the saccharide units include substantially only a single type of group, such as a carboxylic acid group, a nitrile group, a nitroso group or a nitro group.

18. The marked paper product of claim 12 wherein the cellulosic or lignocellulosic material in the paper product is selected from the group consisting of fiber derived from wood, fiber derived from recycled paper, cotton, hemp, linen, rice, sugarcane, bagasse, straw, bamboo, kenaf, jute, and flax, and mixtures thereof.

19. A method of identifying whether a paper product is marked, the method comprising

comparing the functionalization of a sample paper product to the functionalization of a marked paper product.

20. The method of claim 19 further comprising determining the functionalization of the sample paper product using a technique selected from the group consisting of AFM, CFM, ESR and IR.

21. The method of claim 19 wherein comparing comprises comparing the number of carboxylic acid groups present in the sample paper product with the number of carboxylic acid groups present in the marked paper product.

Claims

1. A method comprising:

marking unmarked paper or paper products by irradiation, wherein irradiation comprises exposure to accelerated electrons and/or accelerated particles heavier than an electron and wherein the paper or paper product is irradiated with a total dosage of at least 0.1 Mrad and the electrons or particles have an energy of at least 0.25 MeV.

2. The method of claim 1 wherein the paper or paper product comprises a note.

3. The method of claim 2 further comprising masking an area of the note that is to remain unmarked.

4. The method of claim 3 wherein masking is used to create a symbol on the note.

5. The method of claim 3 wherein masking comprises covering a portion of the note with a radioopaque material during irradiation.

6. The method of claim 2 wherein the note comprises currency.

7. The method of claim 6 wherein the note comprises paper money.

8. The method of claim 1 wherein the particles are positively charged.

9. The method of claim 1 wherein the particles are negatively charged.

10. The method of claim 1 wherein the particles are selected from the group consisting of protons, carbon ions, and combinations thereof.

11. The method of claim 1 wherein irradiation with the particles occurs in a fluid.

12. The method of claim 11 wherein at least some of the particles generate additional chemical species by interacting with the fluid.

13. The method of claim 12 wherein the additional chemical species comprises ozone.

14. The method of claim 1 wherein the irradiation is at a dose sufficient to also crosslink material of the paper or paper products.

15. The method of claim 1 further comprising quenching the paper or paper products after irradiation.

16. The method of claim 15 further comprising masking an area that is to remain unquenched.

17. The method of claim 1 further comprising detecting the marked paper or paper products.

18. The method of claim 17 wherein detecting comprises using infrared spectroscopy.

19. The method of claim 18 wherein detecting comprises using a technique selected from the group consisting of atomic force microscopy, chemical force microscopy or electron spin resonance, and combinations thereof.

20. The method of claim 17 wherein detecting comprises distinguishing the marked paper or paper product from a paper or paper product that has been irradiated under other process conditions.

21. The method of claim 1 wherein the dosage is from about 0.25 Mrad to 5 Mrad.