SUMMARY

The present disclosure~~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.

In one aspect, there is provided a method of making a marked paper product, the method comprising irradiating only a discrete portion of a paper product with at least 0.10 MRad of electron beam radiation, under conditions selected to alter the functionalization of the portion of the paper product so as to mark the paper product.

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

In one embodiment~~aspect~~, ~~the~~ disclosed are~~invention 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.

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.

Irradiation can occur during formation of the paper product. Formation can include amalgamating the pulp material into a wet paper web. Irradiating can be performed on the wet paper web or prior to formation of the wet paper web. Formation can further include drying the wet paper web, and irradiating can occur after drying. In some implementations, powders, granulates, chemical solutions, dyes, inks, or gases can be applied, singularly or in combination, before, during, or after formation of the paper.

In another embodimentaspect, the disclosureinvention features marked paper products that include a cellulosic or lignocellulosic fibrous material containing functional groups not present in a naturally occurring cellulosic or lignocellulosic fibrous material from which the marked paper product was obtained.

The cellulosic or lignocellulosic material in the paper product can be selected, for example, from the group consisting of fiber derived from wood and recycled paper, vegetable fiber materials, such as cotton, hemp, linen, rice, sugarcane, bagasse, straw, bamboo, kenaf, jute, and flax, and mixtures thereof. In some embodiments metal or inorganic fibers can also be included with the cellulosic or lignocellulosic material or included in a portion of the paper product being irradiated.

In a further embodimentaspect, the disclosureinvention features a method of identifying whether a paper product is marked. The method includes comparing the functionalization of a sample paper product to the functionalization of a marked paper product.

In some cases, the method includes determining the functionalization of the sample paper product using infrared spectrometry (IR). The method may include 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.

In some cases, the functionalization is determined using atomic force microscopy (AFM), chemical force microscopy (CFM), or electron spin resonance (ESR).

The paper product may be, for example, currency or a work of art.

In any of the methods disclosed herein, functionalization can include increasing the number of carboxylic acid groups present in the paper. The number of carboxylic acid groups is determined by titration.

The irradiated material can also include functional groups selected from the group consisting of aldehyde groups, nitroso groups, nitrile groups, nitro groups, ketone groups,