

May 13, 1969

S. GELLER ETAL

3,444,084

GARNET COMPOSITIONS

Filed Sept. 30, 1964

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FIG. 1

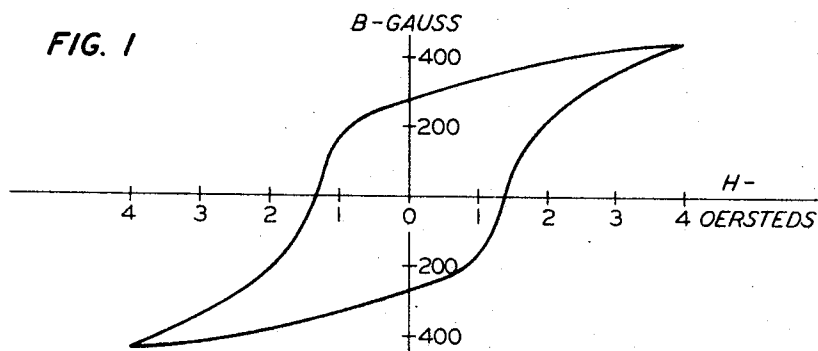


FIG. 2

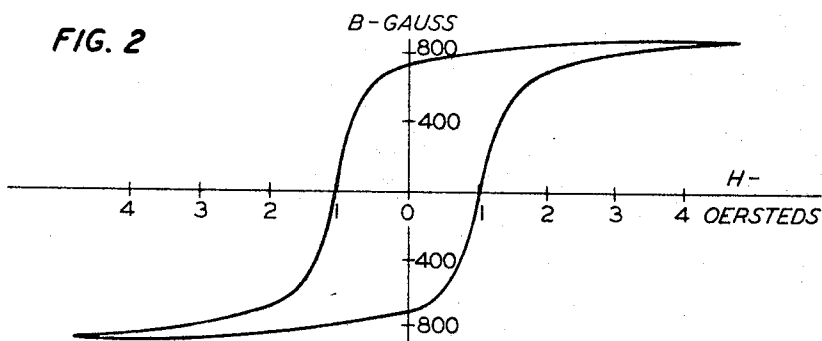


FIG. 3

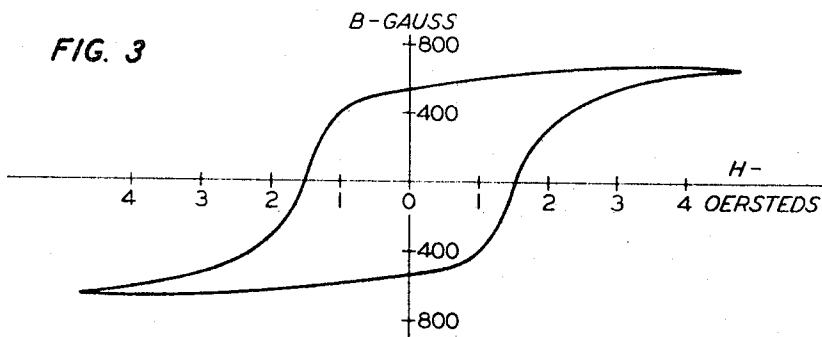
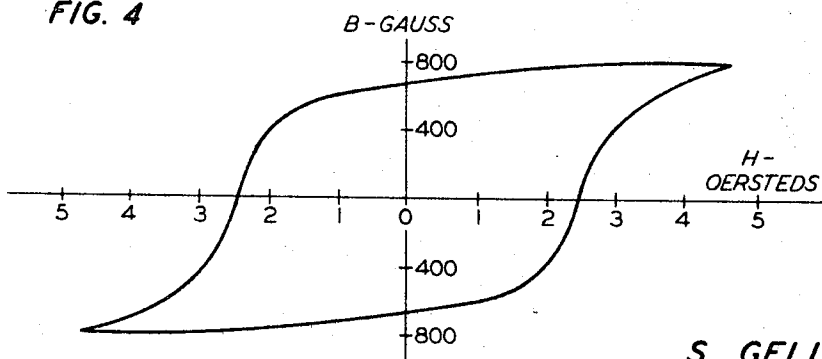


FIG. 4



INVENTORS S. GELLER
E. A. NESBITT
BY *Charles S. Erdig*
ATTORNEY

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FIG. 5

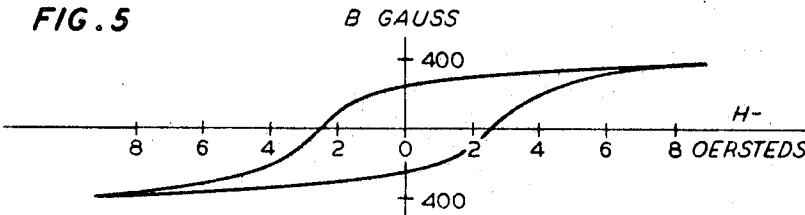


FIG. 6

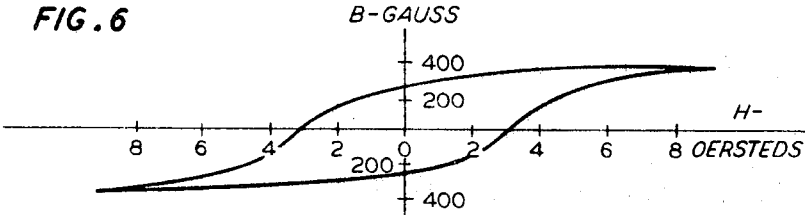


FIG. 7

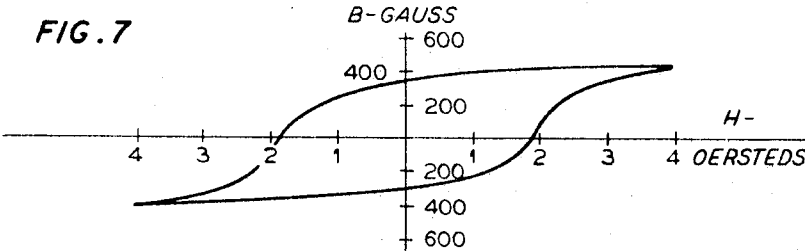


FIG. 8

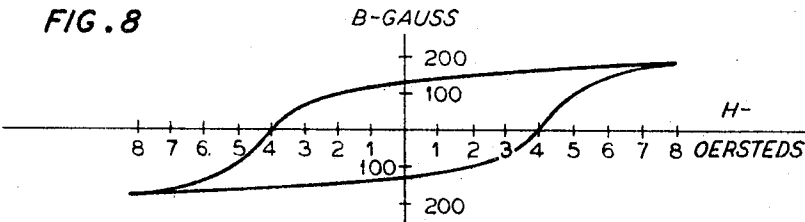
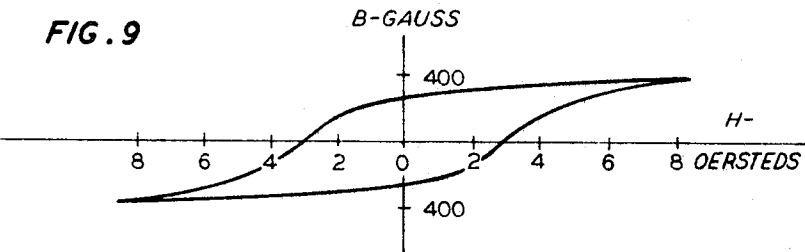


FIG. 9



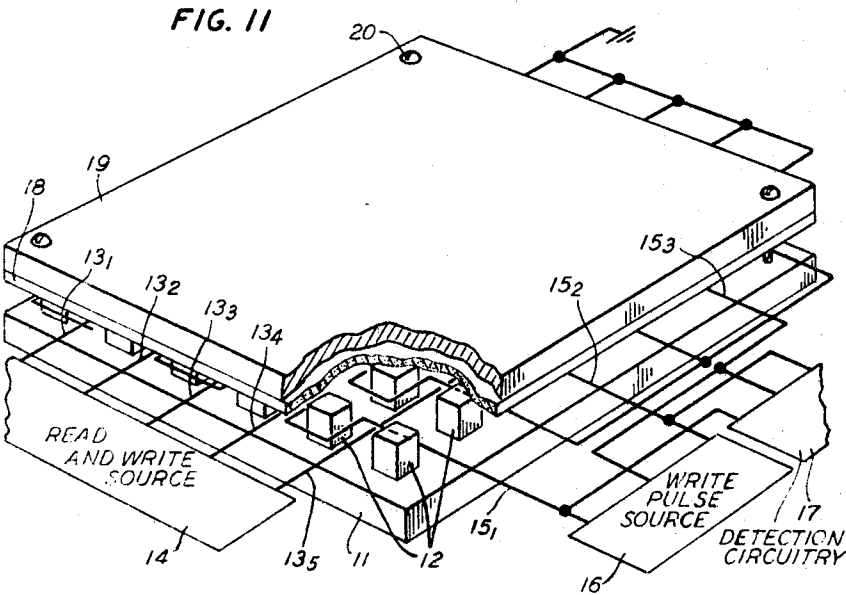
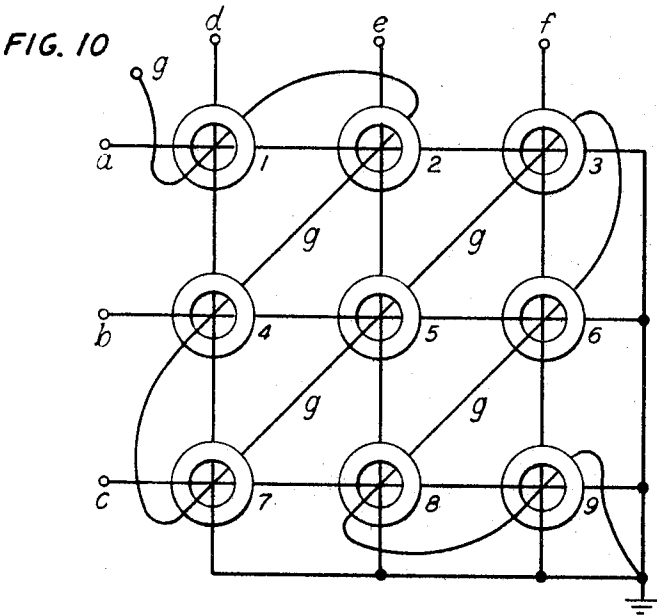
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3,444,084

GARNET COMPOSITIONS

Seymour Geller, Camarillo, Calif., and Ethan A. Nesbitt, Berkeley Heights, N.J., assignors to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

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U.S. Cl. 252-62.57

3 Claims

ABSTRACT OF THE DISCLOSURE

The hysteresis loop squareness ratio of yttrium, iron, garnet (YIG) and related compositions containing limited amounts of gallium and aluminum is improved by partial substitution of europium or terbium for yttrium. Both single crystal and polycrystalline materials are included.

This invention relates to garnet compositions showing enhanced hysteresis loop characteristics and to devices utilizing such compositions.

It is unnecessary to discuss at any length the role played by the hysteresis loop in modern day technology. The remanence of the loop is the memory that serves in all magnetic switching elements from the simple, single element core to the mammoth computer which may use millions of such elements.

While all of the loop characteristics of a material are of concern in the fabrication of any particular device, certain of the characteristics are invariably of importance. Any memory device is dependent on remanence, that is, the magnetization retained by the magnetic element in the absence of an applied field. The ratio of this quantity to the material's saturation, B_R/B_S , the squareness ratio, is a measure of the percentage of the applied field retained upon its removal. It is clear that this is of the nature of an efficiency term, so that a low value of squareness ratio is indicative of wasted energy.

It is well known that squareness ratio is of importance in other design considerations. For example, many composite memory devices operate on the principle of coincident current write. Such elements are operated by use of two associated current windings, which in the write function may each carry currents of a magnitude of the order of half that required to produce a field necessary to magnetically saturate the element. Such elements are switched only when both associated windings are carrying their designated half currents. The more skewed the hysteresis loop, that is, the lower the value of the squareness ratio, the greater the possibility of a half current producing "partial switching." By reason of this condition, a leakage current may, when reinforcing a half current, be adequate to produce switching. Leakage currents increase for closer spacing of elements. It therefore follows that improved squareness ratio permits closer packing of memory elements.

Since a high value of squareness ratio indicates a well-defined easy direction of magnetization which, in turn, signifies a low resistance to domain alignment in such direction, switching speed is expected to be a function of squareness. This is now accepted by workers skilled in the art, and those magnetic memory elements capable of the faster response times which have been reported depend in part for this attribute on the high squareness ratios of the hysteresis loops of the magnetic materials utilized.

Many memory devices utilize magnetic garnet elements based on the stoichiometry $Y_3Fe_5O_{12}$, and sometimes designated yttrium-iron-garnet, or YIG. Such compositions, as well as materials based on such compositions and dif-

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fering therefrom generally by partial substitutions for iron and/or yttrium, generally manifest loop characteristics and saturation values suitable for device applications. One such group of substituted compositions depend for their characteristics on the partial replacement of iron by aluminum or gallium. Such materials show reduced saturation as compared with the prototype YIG and, consequently, permit switching or storage of information with smaller expenditure of energy. While these YAIG or YGaIG compositions have sufficiently square loops for many uses, it is recognized that the squareness ratios are smaller than those of the prototype material.

In accordance with this invention, it has been discovered that partial substitutions of europium and/or terbium for yttrium in YIG, as well as in partially aluminum- or gallium-substituted YIG, results in improved hysteresis loop squareness. The compositional variations so defined, while perhaps of prime technological significance at this time as applied to ceramic bodies, are usefully applied to single crystals of the same compositions. Again from the technological standpoint, prime significance appears to center on the lower saturation materials produced by partial substitution of aluminum or gallium, and such materials constitute a preferred embodiment of this invention. Increasing the hysteresis loop squareness results in the feasible or improved operation of a broad class of magnetic memory elements. Elements utilizing the compositions set forth herein constitute an aspect of the invention.

The materials of this invention may be represented as having a composition within the range defined by:



where R is europium and/or terbium, M is aluminum and/or gallium, x equals from 0.3 to 2.0, and y equals from 0 to 2.0. The choice of europium and terbium in this composition is extremely critical. In fact, no other rare earth which may be substituted for yttrium has been found to share the advantage of either of these elements. The use of aluminum and gallium up to the maximum content indicated is, of course, based on the prior art. These are the reduced saturation materials rapidly gaining acceptance for device use. Since such compositions constitute a preferred embodiment of this invention for certain device uses, and since a significant reduction in saturation is achieved only by use of at least 0.1 atom of aluminum or gallium per formula unit, such a preferred minimum value of y for these purposes is so indicated. The values of x, that is, the limit on europium and/or terbium content, are based largely on experimental work, the results of much of which are reproduced here in graphic form. While lesser substitutions of terbium or europium do produce an improvement in squareness, significant improvement for many device applications is realized only upon incorporation of a minimum amount of 0.3 in the formula. Replacement of two-thirds of the yttrium, that is, use of two atoms of either of these rare earths, still results in significant improvement in squareness ratio. However, since some fall-off in improvement is perceived, the limit of two as the maximum value of x is considered expedient. Variations in the value of y, that is, on aluminum and/or gallium content, are, of course, based on the prior art. It has been observed generally that incorporation of greater than the maximum indicated of either of these metals results in a need for a significant increase in firing temperature in the preparation of the ceramic composition and also results in a concomitant decrease in squareness ratio generally to levels unacceptable for many memory applications. Nevertheless, partial substitution of europium and/or terbium for yttrium results in improvement

in squareness values for compositions containing greater amounts of aluminum or gallium. For the reasons discussed in this paragraph, the composition set forth in the formula above is considered to define only a preferred compositional range in accordance with this invention.

Description of the invention is expedited by reference to the drawing, in which:

FIG. 1 is a BH plot in units of gauss and oersteds, respectively, for a sample of unsubstituted $Y_3Fe_5O_{12}$;

FIG. 2 is a similar plot for a garnet composition containing a small amount of terbium;

FIG. 3 is a similar plot for a europium-substituted garnet;

FIG. 4 is such a plot for a sample of YIG containing a larger amount of europium;

FIG. 5 is such a plot for a europium-substituted yttrium-iron-aluminum garnet composition;

FIG. 6 is such a plot for a composition similar to that of FIG. 5 containing a greater amount of europium;

FIG. 7 is such a plot for a composition similar to that of FIG. 6 containing a still greater amount of europium;

FIG. 8 is such a plot for a composition similar to that of FIG. 5 containing still more europium than the sample of FIG. 7;

FIG. 9 is a similar plot for an yttrium-iron-aluminum garnet composition containing a still greater amount of europium;

FIG. 10 is a schematic representation of a memory array using elements constructed of the materials herein;

FIG. 11 is a perspective view, partly in section, of another design of memory device utilizing a material of this invention.

Materials of this invention may be prepared by any of the several techniques customarily employed either in the ceramic or single crystal field. One method found to produce satisfactory solid solutions (ceramics) involves the preparation of the solid solution directly. In accordance with this method, the necessary chemical elements, for example, in the form of oxides are mixed in stoichiometric proportions. The mixture is then pressed into a pellet and prefixed at a temperature in the preferred range of 1200° C. to 1300° C. for a period of approximately one-half hour. The pellet is then cooled, ground, and remixed, and is then pressed and refired at a temperature of from about 1300° C. to about 1350° C. for a period of approximately one to three hours. Firing, possibly preceded by grinding, may be repeated one or more times to obtain a homogeneous garnet structure or increased bulk density in accordance with the usually practiced procedure. The duration of the firing steps may be increased in accordance with conventional practice.

Single crystals of these compositions may be prepared by spontaneous nucleation from lead-oxide fluxes or from modified lead-oxide fluxes in accordance with the procedures of J. W. Nielsen U.S. Patents No. 2,957,827 and No. 3,050,047, or by use of the J. P. Remeika flux in accordance with his process of U.S. Patent No. 3,079,240. Alternative flux growth procedures, as well as seeded and fusion techniques, are known, and, as would be expected, materials prepared by any of these procedures show improved properties.

For ease of comparison, characteristics plotted on FIGS. 1 through 9 are taken from compositions all prepared in accordance with a ceramic forming technique including firing schedules that are similar for all such samples. All of these samples have been examined by X-ray techniques and found to be homogeneous single phase. It is convenient to consider this series of figures in two subgroupings. Group 1, FIGS. 1 through 5, is based on garnet compositions containing no substitutions for iron. Compositions for this series may, therefore, be represented as $R_xY_{3-x}Fe_5O_{12}$. Terbium is found

to be equivalent to europium in producing improved squareness, and, one of the samples, that plotted on FIG. 2, is of a composition in which yttrium is partially replaced by that element. The compositions of FIGS. 3 and 4 are based on europium substitution. The results are conveniently tabulated below.

TABLE 1

Figure	x	Squareness
1.-----	0	64
2.-----	0.55	80
3.-----	1.35	80
4.-----	1.65	80

It has been noted that reduction of saturation of garnet materials by replacement of nonmagnetic elements, aluminum or gallium, for iron generally results in a sharp decrease in squareness ratio. FIGS. 5 through 9 demonstrate the efficiency of this invention for the retention of usable squareness ratios in such materials. Again for comparison purposes, all samples depicted are of closely related compositions. Dilution of moment is accomplished by replacement of one-half atom of iron by aluminum in the formula unit. For the runs depicted, the same rare earth, europium, in increasing amount from FIGS. 5 through 9, is utilized. The results are summarized in the following table:

TABLE 2

Figure	x	Squareness
5.-----	0.5	60
6.-----	0.75	70
7.-----	1.0	80
8.-----	1.6	80
9.-----	2.0	70

Firing conditions are again similar for the samples represented by FIGS. 5 through 9. Deviation from any of these conditions may increase or decrease saturation and may result in a variation in squareness. Use of terbium rather than europium, while similar in effect, may not be identical in magnitude. Experimental results of which the plotted data are illustrative have established an improvement in squareness for other conditions and other compositions for europium or terbium substitution on a 1:1 comparison. That is, comparison of two samples, one containing three atoms of yttrium per formula unit and the other containing europium or terbium in any amount within the specified range, shows an improvement in squareness ratio where the samples are otherwise identical, that is, same preparation conditions, same degree and type of substitution for iron.

FIG. 10 depicts a bit-organized memory array disclosed and claimed in U.S. Patent 2,825,891, and a more complete operation of this device may be found there. In such a device, cores 1 through 9, all constructed of a garnet composition herein, are interconnected through input windings *a* to *f*, and an output winding *g*, each connected to energizing means, not shown, which windings are single conductors. Each of the cores 1 through 9 is initially in a magnetically remanent condition, with the direction of polarization signifying "0." The writing of a "1," characterized by a remanent condition with an opposite polarization in a given core, is effected by supplying to each conductor associated with said core a current pulse having a value sufficient to produce a flux equal to or slightly more than one-half that required to saturate the core. In the core 8, for example, a "1" is written by supplying a pulse of such magnitude through each of the conductors *e* through *c*, the cores 2, 5, 7, and 9 then being energized only by half currents. This pulse, produced in these four cores, is therefore insufficient to effect a change in direction of polarization. The read-out is effected similarly as described, again using coincident half currents, however of negative direction. This has the effect of switching core 9 to its initial condition, during the course of which a current pulse is induced in read-out winding *g*.

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FIG. 11 depicts a word-organized memory array known as the "waffle iron." This array is constructed of a high magnetic permeability base plate 11 being formed in such fashion as to include protruding posts 12 resembling those of a waffle iron in outward appearance, with a closely fitting overlay sheet of magnetic material 18 of a garnet composition in accordance with this invention positioned across the top of posts 12. The magnetic sheet 18 is advantageously clamped tightly against posts 12 in order to minimize total reluctance of magnetic paths which include both the posts 12 and sheet 18. This clamping is here achieved by means of a metallic pressure plate 19 above the sheet 18 and clamping screws 20 between plate 19 and end portions of the base plate 11. Two electrical conductive paths, any one of windings 13₁ through 13₅, together with any one of 15₁ through 15₃, each connected to energizing means, not shown, are associated with each of posts 12. Writing is accomplished in coincident fashion, supplying half currents in the manner described to a selected pair of such windings. Reading is accomplished by application of a subsequent interrogating signal to a word conductor 13₁ through 13₅, so inducing an output signal in the particular conductor 15₅ through 15₃, the polarity of which is indicative of the stored binary value. A complete description of the operation of such device is set forth in the reference noted above.

Many other devices beneficially incorporating compositions of this invention are known. They include the "Laddic" or U.S. Patent No. 3,040,305, as well as various devices described in U.S. Patent No. 2,736,880. Such devices may utilize open as well as closed flux paths which may have associated with them printed as well as wire or even waveguide conductive paths and may effect partial switching by passage of the current through the magnetic material itself. The suitability of the materials of this invention to all such devices is understood by persons skilled in the art, in consequence of which the description above is considered exemplary only and in no way limiting.

The compositions of this invention have been discussed in terms of the garnet formula. It is known that various additional modifications may be made in such composition to bring about certain desired results. For example,

inert materials such as plastic fillers may be incorporated. Further, it is known that commercially suitable starting ingredients may contain impurities such as to result in as much as one percent by weight of such ingredients in the final composition. Where in the appended claims reference is made to composition in terms of the garnet formula, it is to be understood that all such variations not considered essential to the magnetic characteristic here under consideration, i.e., squareness ratio, are to be considered within the scope of the claims.

What is claimed is:

1. Magnetic material having high values of squareness ratio consisting essentially of the composition which may be represented as:



in which R is at least one rare earth selected from the group consisting of europium and terbium, x is a value of from 0.3 to 2.0, M is a metal selected from the group consisting of aluminum and gallium, and y is a value of from 0.1 to 2.0.

2. Material of claim 1 in which M is aluminum.

3. Material of claim 1 which is polycrystalline.

References Cited

UNITED STATES PATENTS

2,825,891	3/1958	Duinker	340—174
2,938,183	5/1960	Dillon	252—62.57
2,957,827	10/1960	Nielsen	252—62.57
3,003,966	10/1961	Van Uitert	252—62.57
3,040,305	6/1962	Gianola	

OTHER REFERENCES

- Below et al.: Chemical Abstracts, vol. 56, June 1962, p. 13669a.
 Villers et al.: Comptes Rendus, T. 255, No. 7, Aug. 13, 1962, pp. 1196-8.
 TOBIAS E. LEVOW, *Primary Examiner*.
 J. COOPER, *Assistant Examiner*.

U.S. Cl. X.R.

340—174