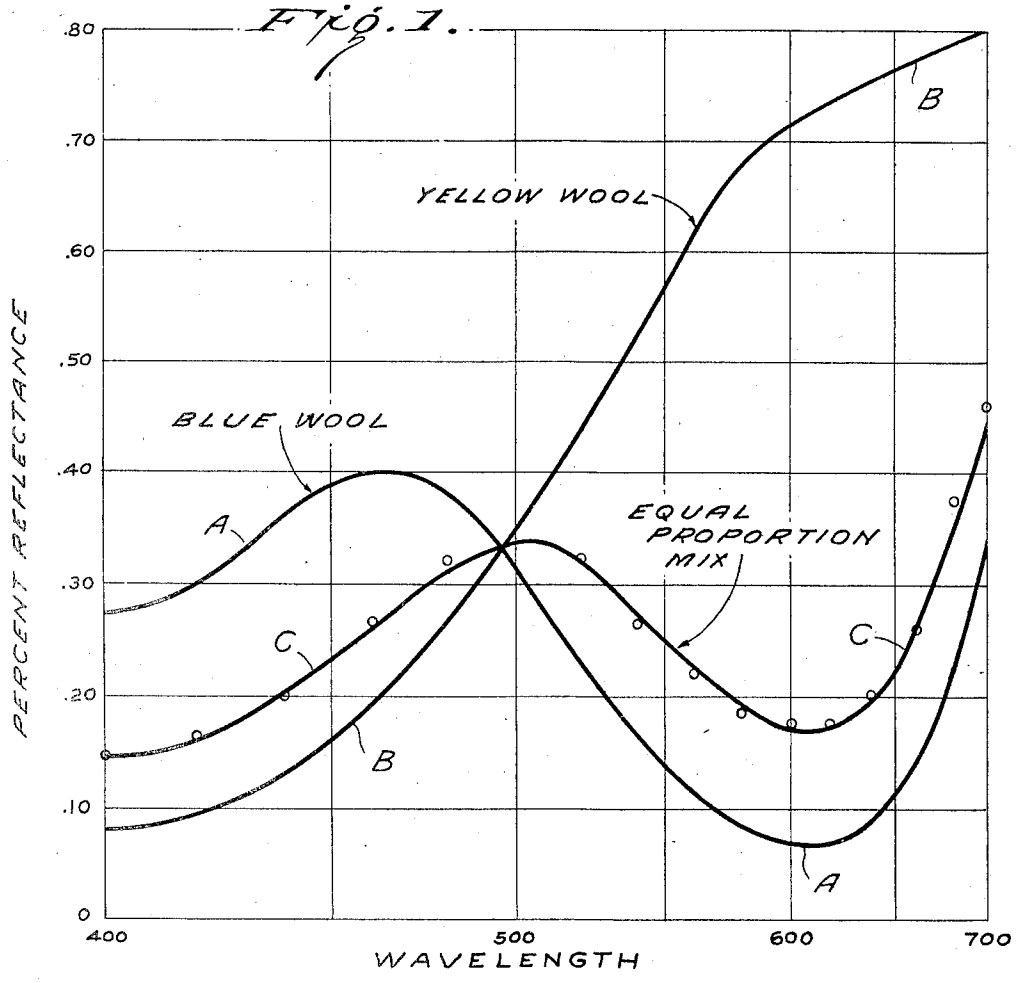
March 21, 1944. E. I. STEARNS, JR 2,344,748

SPECTROPHOTOMETRIC PARTICLE MIXTURE CAM

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Fig. 1.



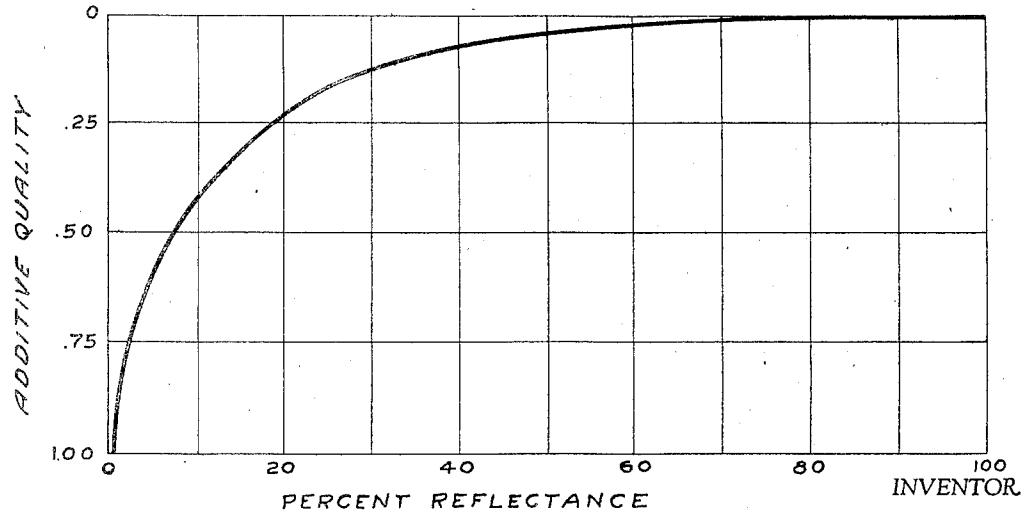


Fig. 2.

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SPECTROPHOTOMETRIC PARTICLE MIXTURE CAM

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Fig. 4.

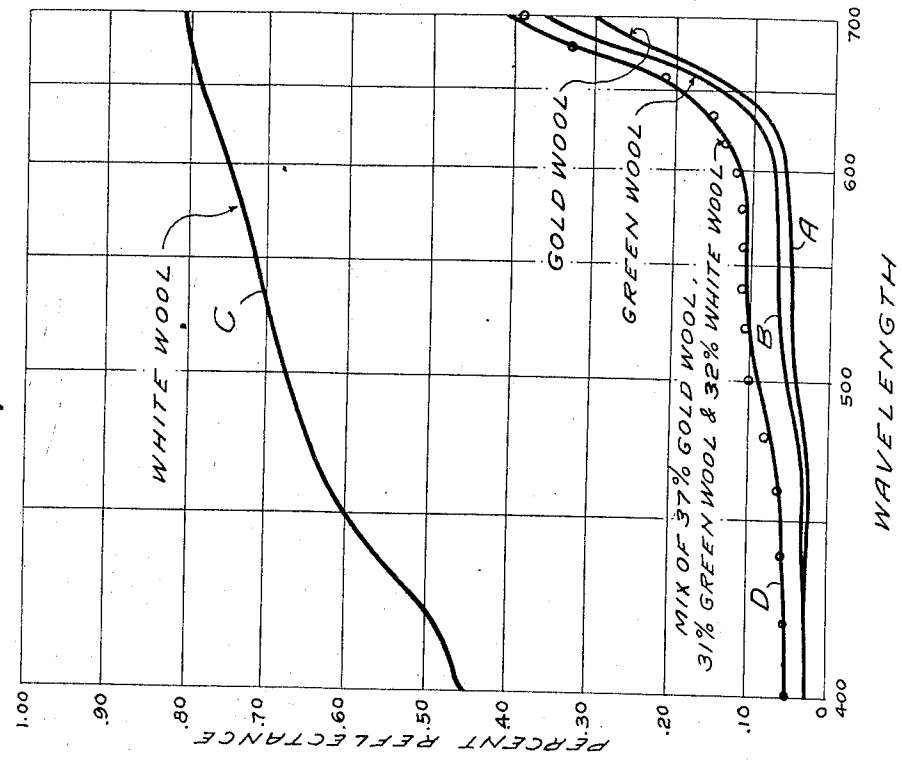
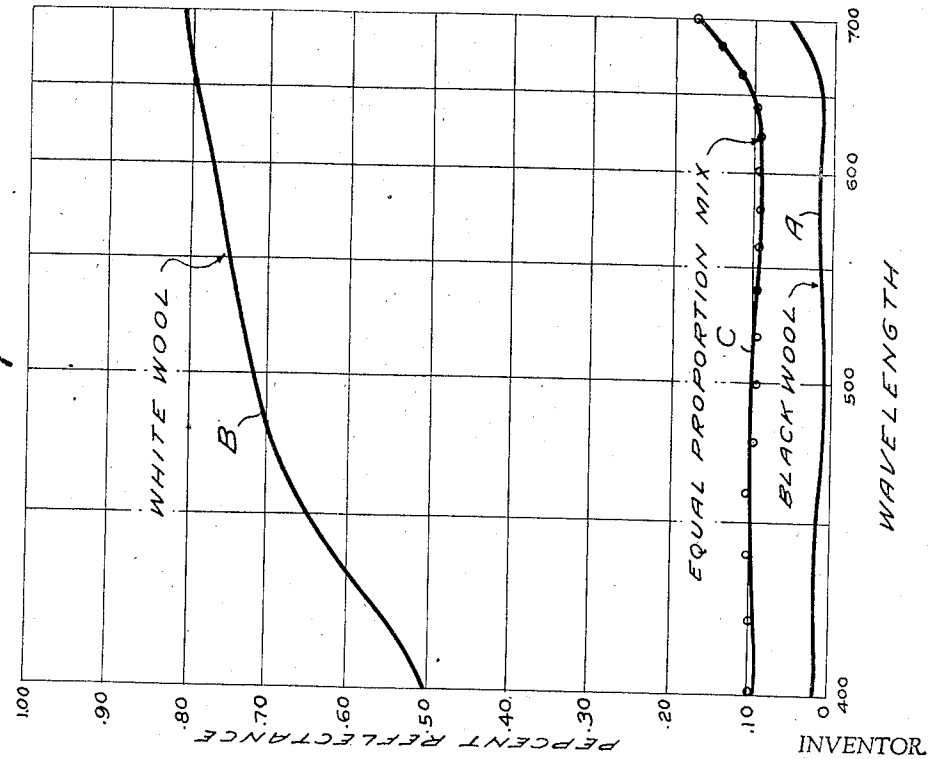


Fig. 3.



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SPECTROPHOTOMETRIC PARTICLE MIXTURE CAM

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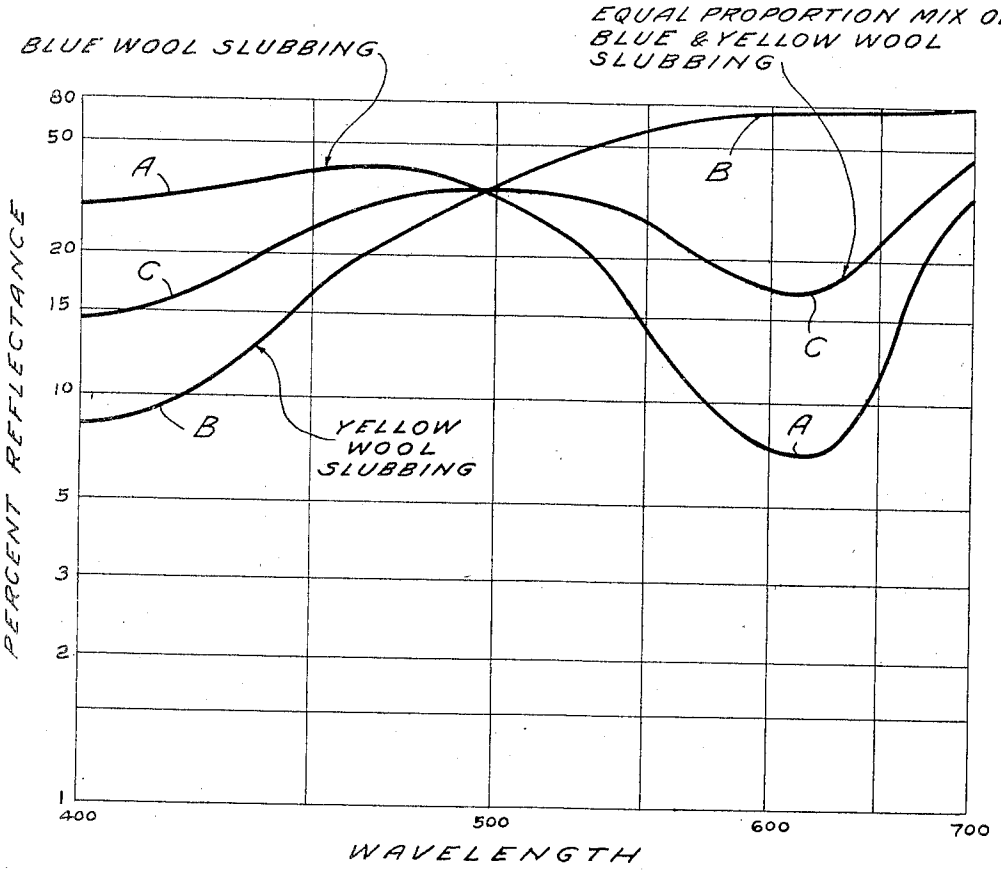


Fig. 5.

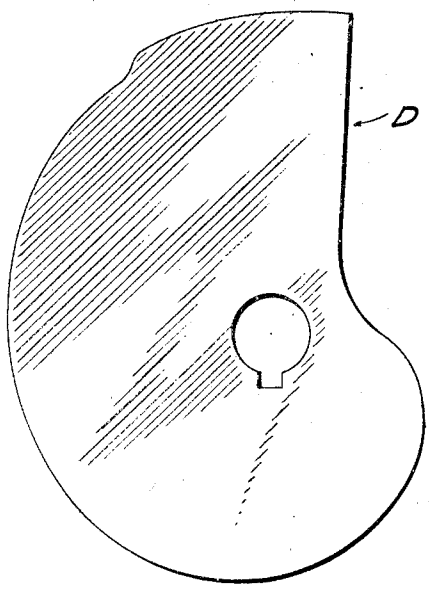


Fig. 9.

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SPECTROPHOTOMETRIC PARTICLE MIXTURE CAM

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Fig. 6.

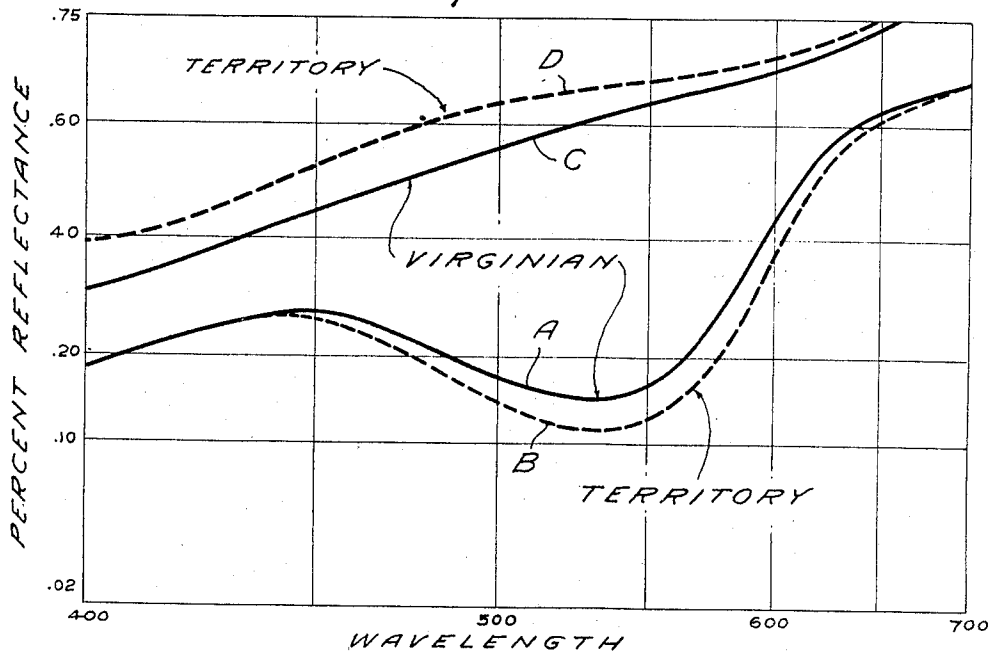
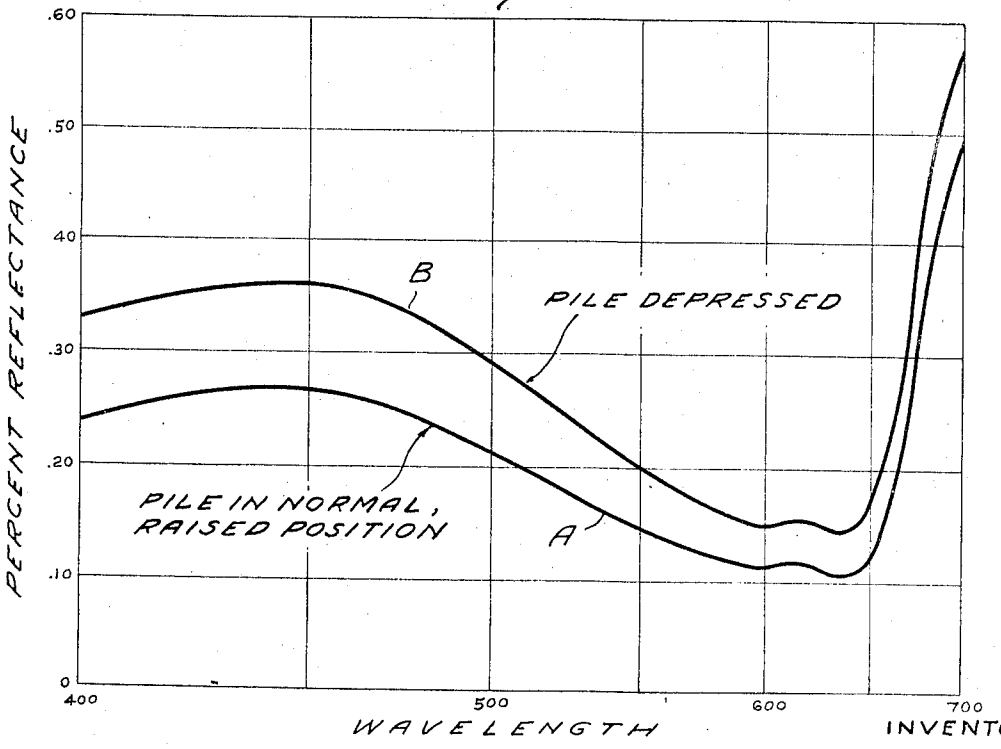


Fig. 7.



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SPECTROPHOTOMETRIC PARTICLE MIXTURE CAM

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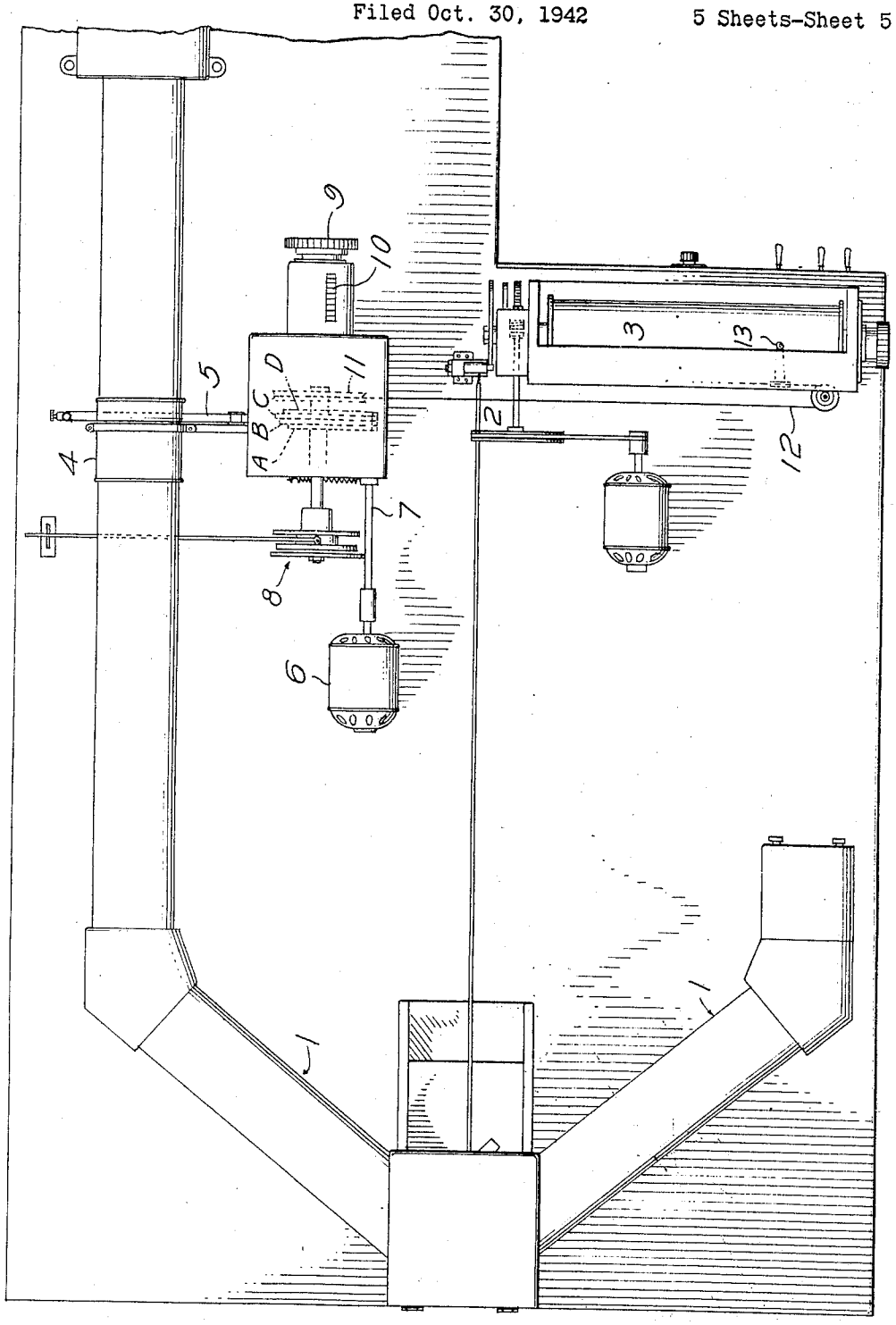


Fig. 8.

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Patented Mar. 21, 1944 2,344,748

UNITED STATES PATENT OFFICE

2,344,748

SPECTROPHOTOMETRIC PARTICLE MIXTURE CAM

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Application October 30, 1942, Serial No. 463,887

6 Claims. (Cl. 234—1.5)

This invention relates to an improvement in flickering beam recording spectrophotometers.

Recording spectrophotometers of the flickering beam type have achieved great practical use by reason of their extreme speed and the fact that they plot directly spectrophotometric curves. Various types of flickering beam spectrophotometers have been designed. They all depend on the use of a photometering element which is connected through suitable linkages, usually involving a drive of varying ratio to a recording pen or other means which is moved over suitable coordinate paper to trace a curve. The drive for the photometering element and recording device is operated by unbalance in the intensity of the two flickering beams after one has been subjected to selective absorption by the sample, either in transmission or reflectance. The amount by which the photometering element has to be moved is the measure of the unbalance. In the visual range and near infrared, the most common machine is one in which the beams are of plane polarized light and are flickered in opposite phase, the beams then entering an integrating device provided with photocells or similar photoelectric means and high gain amplifiers which respond to fluctuations at flicker frequency. Other devices of flickering beam spectrophotometers for infrared and similar use employ opposed thermocouples or other radiation detectors. A typical flickering beam spectrophotometer of the visual type is described and claimed in the patent to Pineo, No. 2,107,836 dated February 8, 1938. In a flickering beam spectrophotometer involving polarized light such as that described in the Pineo patent above referred to, photometry is generally by the polarized element and it is necessary to introduce in the linkage of the photometer of the recording device a suitable drive of varying ratio, in a commercial machine usually a cam because the change in relative intensity of beams is proportional to the square of the tangent of the angle through which the spectrophotometer is turned and this is, of course, not a linear function. An ordinary tangent squared cam plots curves on rectangular coordinate paper which gives a percentage reflectance or transmission directly, the same cam being usual for both types of recording.

The simple flickering beam spectrophotometer described above was open to some objections when used in comparing color mixtures, the concentration of which was unknown because the shape of curves varied with concentration, the latter factor being a variable in the exponent of the formula governing absorption of the light by transmission or reflectance. It was found that by using varying ratio drives corresponding to certain mathematical functions, it was possible to plot on a particular type of coordinate paper curves of transmission or reflectance which would be invariant in shape with changes in concentration, such changes effecting merely a linear displacement of the ordinates of the curves. Recording spectrophotometers having varying ratio drive connections between the photometering element and recording element are described and claimed in the patents to Pineo No. 2,176,013 dated October 10, 1939 and 2,218,357 dated October 15, 1940. A spectrophotometer provided with cams designed in accordance with the latter patents solved the serious problems presented by the identification and matching of colors produced by different mixtures of the dyes.

The cams described in the later Pineo patents deal with colors which contain extremely fine division of colored particles. In many cases they are of molecular size, and in other cases they are far below limits of optic resolution. In the case of colored areas which are very large in comparison to a wave length of visible light, such as for example checkerboard patterns where the individual squares are clearly distinguishable by the eye, the mixture of different colors produces curves which may be predicted by linear interpolation with an ordinary linear spectrophotometer such as described in the earlier Pineo patent. In between these two limits, however, there are a number of important coloring problems for which cams capable of producing curves having shapes predictable by linear interpolation are needed. These are represented by mixtures of fibers, the least dimensions of which are smaller than the squares of a gross checkerboard pattern, but are materially larger than the dimensions of a wave length of light, and hence act optically partly as separate entities, whereas with a molecular dispersion, such as is obtained with dyeings, the individual colored particles are not optically resolvable and hence absorb color according to statistical laws. The problem of fibers is frequently encountered where different colored yarns are mixed in fabrics, or where a fabric may have a fiber pile as in the case of some velvets. No reflectant or transmission curves from spectrophotometers hitherto known give any information which can permit a rapid prediction of the shade obtained by various mixtures of colored yarns and matching of such mixtures has hitherto been largely a problem of cut and try.

The tremendous advantage in speed which the improved spectrophotometer permitted in the case of mixtures of colors on the same material was not available.

An example of the difficulties encountered may be taken by considering mixtures of wool dyed with a color having a given reflectance at a certain wave-length. Let us assume that one fiber has a reflectance of 10% at a given wave-length and another fiber 50% at the same wave-length. When equal quantities of the same fiber are mixed either in the form of slubbing or in the form of a mixed woven cloth, the reflectance at that wave length will not be 30% as would be the case if the measurements were averaged, but is found experimentally to be around 19%.

According to the present invention it has been found that a relation exists by which the additive quality of various colored fibers, or colored particles of comparable size, may be determined, and as this formula is capable of graphical representation it is possible to design cams for inclusion in the spectrophotometer in a manner similar to the cams in the Pineo patents, so that the spectrophotometer will automatically draw curves of colored fibers which permit prediction of reflectances of mixtures with various proportions of fibers.

It has been found that particles having a smaller dimension comparable to fibers have an additive quality which follows the following formula:

$$Y=\frac{100-R}{b(R-1)+1}$$

in which R is the body reflectant percentage and b is a constant greater than zero and less than 1. For practical purposes the constant b varies from about 0.05 to 0.5. For wool fibers b should be about 0.15, while cotton, hemp, jute, silk, linen and rayon fibers require slightly different values, although in many cases the same cam useful for wool may be employed for these fibers. Compressed cork dust, or sawdust, requires lower values of b, while paints made from coarse particles will require somewhat higher values.

It is not intended to limit the present invention to a particular theory of action, and it has been impossible to determine whether the hyperbolic relationship between the additive quality and body reflectance represents an underlying physical law. In fact, the evidence available indicates that the factors involved are probably much more complicated, and the hyperbolic relationship which can be easily used in calculating a cam contour is a close approximation. This is substantiated by the fact that slight but not significant departures are to be noted when wool mixtures are calculated from curves of the components drawn with the hyperbolic cam. The departure on an absolute basis is extremely slight, the error not exceeding 2% and usually being much less, of the order of magnitude of ½–1% or less.

In common with the experience with cams for drawing curves of invariant shape with concentration for dyeings they are not designed for extremely high reflectances although the usefulness does not cease at as low a point, reflectances up to 80% being satisfactorily handled by the hyperbolic cam, whereas the accuracy of the cams in the later Pineo patents falls off quite rapidly above 70%. The lack of complete accuracy at high reflectances is a matter of little moment in the visible spectrum, since there is no undyed wool known having a reflectance greater than 80%, and the useful range of the instrument covers substantially all practical problems. As has been pointed out above, the present invention is directed to a practical machine having the requisite degree of accuracy through practical measured ranges and is not intended to solve underlying fundamental physical problems.

The invention will be described in greater detail in conjunction with the drawings in which:

Fig. 1 is a series of three curves of two dyed wool samples and the resulting mixture on an ordinary recording spectrophotometer of the flickering beam type;

Fig. 2 is a curve of the additive quality of the dyed yarn plotted against reflectance;

Fig. 3 is a series of curves of two samples of colored wool and a curve comparing the predicted and experimentally determined spectrophotometric curve of the mixture;

Fig. 4 is a similar set of curves for three colored wools with the curve for the mixture;

Fig. 5 is a series of curves plotted on special coordinate paper by a recording spectrophotometer having a varying ratio drive in accordance with the present invention;

Fig. 6 is a similar set of curves plotted for different types of wool;

Fig. 7 is a series of curves in pile fabric with normal and depressed pile;

Fig. 8 is a semi-diagrammatic illustration of a flickering beam spectrophotometer of conventional type employing the varying ratio drive of the present invention; and

Fig. 9 is a detailed view of a typical cam according to the present invention.

The additive property of dyed wool fibers which permits linear addition of curves when empirically determined is represented in the following table, the additive quality Y being plotted against body reflectant R:

Table 1

R	y	R	y	R	y	R	y
1.0	100	5	57	16	29	60	3
1.5	87	6	53	18	26	70	1
2.0	79	7	50	20	22	80	0
2.5	73	8	47	25	17	100	0
3.0	63	9	44	30	14	---	-
3.5	65	10	42	35	11	---	-
4.0	62	12	37	40	8	---	-
4.5	59	14	32	50	5	---	-

The curve corresponds closely to the hyperbola when B is equal to 0.15, and this curve is shown in Fig. 2. The accuracies with which predicted shades of wool mixtures may be determined by the additive quality referred to above is shown in Figs. 1, 3 and 4. In each of these figures spectrophotometric curves drawn on an ordinary recording spectrophotometer are present giving the curves for blue wool and yellow wool at A and B in Fig. 1, black wool and white wool in A, and B of Fig. 3, and gold wool, green wool and white wool in curves A, B and C in Fig. 4. The curve y in Figs. 1 and 3 is the curve of a 50/50 mixture of the two colored wools and the curve D is the spectrophotometric curve of the mixture obtained by mixing 37% of A, 31% of B and 32% of C in Fig. 4. In each of these figures, a series of circles are shown which are calculated points using Table 1. It will be noted that these points fall very closely on the measured curve for the shade mixtures, differences being within the ex-

perimental error of measurement which with mixed dyed fibers also gives a slightly lower degree of accuracy than uniform surfaces.

The importance of predicting shades of mixed dyed fibers is well brought out in Fig. 4 which is a problem of making color in Army uniforms and equipment. The problem is particularly difficult because fabrics produced by mixtures of colored fibers are often not completely uniform, the effect being discontinuous and giving certain well known texture or pattern effects in mixed goods. It is extremely difficult to make accurate matches, especially in that shown in Fig. 4 and large amounts of rejections have resulted because of the impossibility of predicting the shade obtained with various mixtures directly from the spectrophotometric curves of the dyed yarns themselves.

The cam in the case of flickering beam spectrophotometers employing polarized beams, must include in its profile also the function which relates the angle of rotation of the polarized angle to the degree of change of intensity of the beams, that is the tangent squared proportional function referred to above in conjunction with the first Pineo patent. When such a cam is employed and a plot is made on suitable coordinate paper, curves for the components of mixture represented in Fig. 1 appear as in Fig. 5. It will be noted that the curve C for the equal blend is exactly in the middle between curves A and B whereas on an ordinary machine as is shown in Fig. 1 the curve C bears no useful relationship to curves A and B except the obvious one that the blend must be intermediate in reflectance between the two components.

In Fig. 8 there is shown in diagrammatic form a typical flickering beam spectrophotometer of the type described in the Pineo patents above referred to comprising a double monochromator 1 driven through the drive 2 from a driving mechanism (not shown) for rotating a recording drum 3. Light from the exit slit of the monochromator passed through a Rochon photometric prism mounted in a rotatable sleeve 4 moved by the cam follower rod 5. The photometering motor 6 is driven in the output of the high gain amplifier (not shown) operating as in an ordinary spectrophotometer, drives a shaft 7 which in turn drives a slidable reduction gearing 8 of the design described and claimed in the Pineo patent application Serial No. 441,030 filed April 29, 1942 above referred to. The reduction gear drives the shaft on which are mounted four cams, A, B, C, and D. Cams A, B, and C are percentage reflectance, transmission and invariant curve shaped reflectance respectively and cam D is a cam plotted with the additive quality according to the present invention. These cams can be successfully engaged with the cam follower rod 5 in connection with the knurled nut 9 which serves to turn the shaft on which the cams are mounted at the point at which all cams have common elevation and can then be used to move the shaft axially and can thus be used to engage the cam follower. The cam engaged is shown by suitable scale and pointer through a window 10.

Pulley 11 is mounted on the shaft on which the cams are mounted and moves the recording pen 3 by means of the driving cord 12.

Operation of the machine as a spectrophotometer is unchanged and proceeds in the conventional manner as described and claimed in the Pineo patents referred to above.

A curve in terms of the additive quality is also useful to determine shades obtainable with different types of wool. Four such curves are shown in Fig. 6, the two curves for the undyed wool being at C and D and the corresponding curves with the same dyebath concentration appear respectively at A and B. It will be noted that the mixture of wools required to produce a given shade can be determined by means of curves drawn by machine having a cam according to the present invention.

Fig. 7 shows a different application of the additive quantity in which a pile fabric is dealt with. The two curves show the pile in normal raised position at A and in depressed position at B. Any intermediate condition can be determined by curves plotting the additive quantity which is of interest in many applications of crease-proofing agents and the like to pile fabrics and the evaluation of pile depression in rug soiling.

Many other applications of the machine of the present invention are possible, but its primary field, of course, is in the prediction by matching of shades to be obtained with the mixtures of dyed yarns.

In Fig. 8 there has been described a spectrophotometer which in addition to the cam of the present invention is provided with other cams for normal operation and the improved means for shifting these cams into contact with a cam follower. Such a spectrophotometer presents considerable advantages in general research work as it performs not only the function of the present invention but can also be used for spectrophotometric measurements. The present invention is, however, not limited to a spectrophotometer which combines the functions of an ordinary spectrophotometer with those of the present invention, this being merely a preferred modification. It is an important advantage of the present invention that the ordinary operation of a recording spectrophotometer is not changed and that it is possible to apply the present invention to existing machines by the simple addition of another cam. This is of importance as there are many existing machines and they are relatively expensive. The possibility of applying the present invention to them without change in their essential operation is an important economic advantage.

I claim:

1. In a recording spectrophotometer of the flickering beam type for measuring the reflectance of a colored sample, in which a photometering element is moved to control the relative intensities of the beams and thereby to compensate for the reflectance of the colored sample and in which a recording device is actuated to move a recording surface in accordance with wave length or frequency of monochromatic light being introduced into the spectrophotometer, the improvement which comprises a drive linkage between the photometering element and a recording means operating on the recording surface, said linkage including a drive of varying ratio, the ratio of variation of said drive being such that the value recorded is substantially proportional to

$$\frac{100-R}{b(R-1)+1}$$

where R is percent body reflectance and b is a constant having a value between 0 and 1.

2. In a recording spectrophotometer of the polarization flickering beam type for measuring

the reflectance of a colored sample in which a photometering element is rotated through an angle α to control the relative intensities of the beams and thereby to compensate for the reflectance of the colored sample and in which a recording device is actuated to move a recording surface in accordance with wave length or frequency of monochromatic light being introduced into the spectrophotometer, the improvement which comprises a drive linkage between the photometering element and a recording means operating on the recording surface, said linkage including a drive of varying ratio, the ratio of variation of said drive being such that the value recorded is substantially proportional to

$$\frac{1-\tan^2\alpha}{b(100\tan^2\alpha-1)+1}$$

where b is a constant having a value between 0 and 1.

3. In a recording spectrophotometer of the flickering beam type for measuring the reflectance of a colored sample, in which a photometering element is moved to control the relative intensities of the beams and thereby to compensate for the reflectance of the colored sample and in which a recording device is actuated to move a recording surface in accordance with wave length or frequency of monochromatic light being introduced into the spectrophotometer, the improvement which comprises a drive linkage between the photometering element and a recording means operating on the recording surface, said linkage including a drive of varying ratio, the ratio of variation of said drive being such that the value recorded is substantially proportional to

$$\frac{100-R}{b(R-1)+1}$$

where R is percent body reflectance and b is a constant having a value between 0.05 and 0.5.

4. In a recording spectrophotometer of the polarization flickering beam type for measuring the reflectance of a colored sample in which a photometering element is rotated through an angle α to control the relative intensities of the beams and thereby to compensate for the reflectance of the colored sample and in which a recording device is actuated to move a recording surface in accordance with wave length or frequency of monochromatic light being introduced into the spectrophotometer, the improvement which comprises a drive linkage between the photometering element and a recording means operating on the recording surface, said linkage including a drive of varying ratio, the ratio of variation of said drive being such that the value recorded is substantially proportional to

$$\frac{1-\tan^2\alpha}{b(100\tan^2\alpha-1)+1}$$

where b is a constant having a value between 0.05 and 0.5.

5. A recording spectrophotometer according to claim 3 in which b is approximately 0.15.

6. A recording spectrophotometer according to claim 4 in which b is approximately 0.15.

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