# CHAPTER V

# ELECTROLUMINESCENCE

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## 5.1 INTRODUCTION

Substances, which emit electromagnetic radiation (visible or near visible) due to the application of an electric field (AC or DC) are called electroluminescent materials and the phenomenon involved in the emission of the light is termed as electroluminescence (EL.) Studies of voltage and frequency dependence of time averaged electroluminescent brightness and brightness waveforms are the important means to understand the mechanism of electroluminescence. In the present studies on voltage and frequency of time averaged electroluminescent brightness are studied so as to gain the information about -

a) effect of activator on EL behaviour

b) Voltage dependance of EL brightness

c) Frequency dependance of EL brightness

d) Mechanism of EL

e) Kinetic involved in EL process.

## 5.2 THEORETICAL BACKGROUND

### 5.2.1 Relation betwen brightness and applied voltage :

The exciting voltage affect the electroluminescence brightness. A variety of mathematical forms proposed by various workers are presented here and they appear to be a considerable disagreement as regards the exact quantitive relationship.

In 1936, Destrain (45) observed that the time average of the emission intensity of electroluminescent.Zinc sulphate phosphor increases exponentially with increasing amplitude of exciting alternating field. The first relation proposed by him is -

$$B = a \exp. (-b/v) \qquad .. \quad (5.1)$$

where B and v are brightness and voltage respectively and a and b are constant independent of v but dependent on temp. type of phosphor and frequency of applied voltage. The relation is amenable to simple theoretical interpretation (5). Later, Distrian (9) changed this to -

$$B = a V^n \exp. (-b/v) \quad .. \quad (5.2)$$

where 'n' being a constant, for single crystal of ZnS, a relation,

$$B = aV^n \exp. (-b/\sqrt{v}) \quad .. \quad (5.3)$$

is given by Alfrey and Taylor (1). This equation with n = 1 is found to be hold good for ZnS:Mn films (34). The equation (5.3) with n=0 reduces to

$$B = a \exp. (-b/\sqrt{v}) \quad .. \quad (5.4)$$

This equation was employed by Alfrey and Taylor (17) and Zalm et al. (41, 42) Zalm and his co-workers (41, 42) have reported that this equation is valid over seven decades of brightness for micro-crystalline ZnS phosphors. The equation (5.4) holds only at low voltage this is shown by Thronton and others (35, 2, 36). At high voltage the equation,

$$B = a \exp . (-b / v) \quad .. \quad (5.5)$$

works more satisfactorily.

Lehmann (24) found the emission of individual particles to obey equation (5.5) and showed that summation of the output of large number of particles leads to the normally observed equation (5.4).

A relation similar to equation (5.5) viz.

$$B = a \exp. (-b/V + V_0) \quad .. \quad (5.6)$$

was first proposed by Destrian and Ivey (10) and subsequently used by Morehead (29) with some success in ZnS and ZnS:Cu:Cl.

For microcrystalline ZnS activated with Cu, Howard et al (16) and Lehmann proposed

$$B = a\,v\ \exp.\ (-b/v+v_0) \quad .. \quad (5.7)$$

where B and $V_0$ increases slowly with frequency.

On the basis of exhaustion barrier theory Taylor (37) deduced the following relation-

$$B = B_0\ \exp.\ \left(-\left(\frac{V_0}{V}\right)^{\frac{1}{2}}\right) \quad .. \quad (5.8)$$

where as on the basis of impact ionisation mechanism Nagy (30) derived the following relation -

$$B = a\ \exp.\ (-b/(1+cv)^2) \quad .. \quad (5.9)$$

Luyckz and Stokkink (26) reported a relation $B = a\ \exp.\ (bv)$ ..(5.10) for microcystalline ZnS:Mn Ihrman and Raybold (17) have suggested the power law relation,

$$B = a(V - V_0)^n \quad .. \quad (5.11)$$

For ZnS phosphors with n = 3. A similar expression with $V_0 = 0$ and n = 2.5 was given by Diemer (11) for single crystals of ZnS and wasfound to be valid at high voltages over five decades of brightness. Halsten and Kollar (18) used equation (5.11) with $V_0 = 0$ and n = 7. Zalm et. al (43) used it with n = 3.5. Gaur and Ranade (14) used this equation with V = 0 and n = 6.5 for CaS:Ag phosphors. Lawangar and Pawar (27) used equation (5.11) with Vo = 0 for CaS:Bi:Pd phosphor.

On the basis of Piper and Williams theory Howard et.al(16) obtained another relation as -

$$B = a\ v^{3/2}\left(1-\frac{3v^{\frac{1}{2}}}{c}\right)\ \exp.\ (-c/v^{\frac{1}{2}}) \quad .. \quad (5.12)$$

with a and c as constant.

Vlasenko and Popkov (39) have found another empirical formula for film panels, viz,

$$B = g \exp. (\sqrt{v}/h) \quad .. \quad (5.13)$$

where g and h are constants. Chen and Yu(6) have shown that EL emittance of thin panels depend on various parameters, such as composition and aging of panel and applied voltage. They have studied evaporated film panels of ZnS:Mn, Cu, Cl and have given an empirical formula,

$$B = A. \exp. \left(-\frac{G}{F} + \sqrt{v}\right) \quad .. \quad (5.14)$$

where A, G and F are functions of operating time and can be regarded as constants during any measurement of EL emittance,

Z.porada (31) applied the EL model suggested by Alfrey and Taylor (3) to explain the observed EL emission excited by high energy electrons in the strong electric field of the metal semiconductor junction and arrived at the equation,

$$B = Bo \exp. (-A/F) \exp. (-\alpha / \sqrt{v}) \quad .. \quad (5.15)$$

where Bo is a constant independent of units in which B is expressed. A is a parameter dependent on the technological conditions under which samples are prepared and temperature, f is frequency and $\alpha$ is a parameter dependent on the values of the critical intensity of the electric field causing ionisation by luminescent center with v as applied voltage.

5.2.2 Relation Between Brightness and Frequency

The EL brightness is the function of applied voltage and also of the frequency. Various relations between brightness and frequency given by different workers are given below :

Curie(7, 8) has derived an expression on the assumption that there exists a bimolecular process of recombination of electrons with recombination centres and that the same number of excited centres are produced per cycle. The expression is,

$$B = Bo. \frac{n_o^2}{(1+ \frac{n_o \alpha}{2f})} \quad .. \quad (5.16)$$

where $\alpha$ is recombination coefficient $n_o$ the initial concentration of free electrons in the conduction band, f the frequency of applied field and Bo a proportionality constant.

Thorntor (35) considering the recombination rate as determined from the electrons released from traps and controlled by electric field obtained,

$$B = No\ f( 1 - exp.\ (-A/F) \quad .. \quad (5.17)$$

where No is the number of excited centres for each half cycle, assumed to be constant,

$A = \int_0^{2\pi} exp.\ (av\ sin\ x)\ .\ dx$ with $x = wt$ is field dependent factor which increases with voltage. Alfrey and Taylor (3) has given a relation,

$$B = B_oP\ exp.(-P/4f)\ exp.\ (c / \sqrt{v}) \quad .. \quad (5.18)$$

where C is constant, v being the applied voltage and p the rate constant for thermal emptying of traps and is given by

$$p = S.\ exp.\ (-E/KT) \quad .. \quad (5.19)$$

Here s and E represents the frequency factor and trap depth resp. Zalmp (44) showed that the light emission during each cycle of the applied voltage is not constant but is dependent on the frequency of the applied field. He gives a relation,

$$B \propto exp.(- constant / \sqrt{v}) \quad .. \quad (5.20)$$

where $V = F(f, t)$, f being frequency and t the time. Thus light emitted for a cycle is inversely prportional to f so that the total light emitted per unit time is independent of frequency, which is contrary to the observation.

Zalm considers that the actural voltage across the cell may be given by

$$W R C V_o / \sqrt{1 + W^2R^2C^2} \quad .. \quad (5.21)$$

where Vo is amplitude of the applied voltage to the whole system by capactor and EL cell. If $RC \gg \frac{1}{w}$, the total voltage across the cell and consequently the lumineous emittance is independent of frequency, while with $RC \ll 1/w$, the emittance increases more than linearly with the frequency. It is thus possible to describe any frequency dependence with a suitable distribution in RC values of the system.

Johnson, Piper and Williams (21) deduced the brightness frequency relation by considering both excitation and recombination process. Johnson et al found -

$$B \propto (1 - a(1 - \exp.(1 - 1/2f\,\tau_2).\exp.\left(- \frac{1}{2f\,\tau_1}\right) \quad .. \quad (5.22)$$

where a is constant, $\tau_1$ is the relaxation time of the excited electrons returning to empty luminescence centres and $\tau_2$ is the time constant of creation of primary electrons.

Chan and Yu (26) have empirically suggested that the El-emittance (B) varies with frequency (f) of applied Sinusoidal field as-

$$B = Bs - Bm.\exp.(-f/fc) \quad .. \quad (5.23)$$

where Bs, Bm and fc are constants ($Bs \neq Bm$). The equation indicates that B approaches a saturation value Bs when $F \gg fe$ and a linear relation between B and f when $f \ll Fc$

### 5.2.3 Brightness Waves

Brightness wave is the variation of EL brightness with time, during the applied a.c. voltages. Besides it is graphic indication of phase relationship of light component (to the applied voltage) on a double beam cathode ray osciallosccope. The shape of brightness waves depends upon the field intensity, frequency and the direction in which the light output is observed. It also depends on the nature of activators, and the spectral characteristic of the detector (PM tube). The existance of brightness waves and the fact that its frequency is twice the frequency of applied voltage, were first reported by Destriau(12, 13) in year 1937.

In general the brightness wave exhibit two main or the so called, 'primary' peaks during each cycle of the applied voltage. Some phosphors however, show additional much smaller or minor peaks referred to as 'secondary' peaks. The existence of secondary peak is related to the electrons which recombines with luminescence centre after a delay resulting from trapping (5,19). The prominance of primary peaks than the secondary peaks at the applied voltages suggests that in the phosphor deeper trap levels are less in number. Moreover, absence of secondary peak suggests that the electron traps are located close to the luminescence centres (19,22, 17).

### 5.2.4 Efficiency of Electroluminescence

The lumineous efficiency (lumens/Watt) of electroluminescence of powdered crystal phosphor embedded in an insulating medium and excited by a.c. fields, depends on the quality of phosphor, the EL-cell design and the conditions of excitation.

Lehmann (28) has given empirical relation from efficiency of on EL phosphor namely,

$$\eta^2 = c^2 \; (B/v^{4}) \qquad .. \qquad (5.24)$$

where C is constant. From this eqn. efficiency increases with brightness increases faster than the fourth powerof the applied voltage. The efficiency is seen to be approximately independent of the frequency of excitation but depend upon the magnitude of the applied voltage. By Lehmann (28) relation, the luminescence efficiency can be calculated -

$$\eta = \frac{B}{W} = \frac{B/F}{av^2 (K''_o \; + b(B/f)^{\frac{1}{2}}} \ldots \qquad (5.25)$$

where $\overset{*}{Ko}$ , a and b are constants, the value of a and be are to be taken from the work of Schwertz et. al. (38) while $\overset{''}{Ko}$ is taken to be unity.

## 5.3 RESULT AND DISCUSSION

### 5.3.1 Voltage Dependence of EL-brightness

Studies of voltage and frequency depend~~a~~ence have been carried out in the voltage range from 0 to 950 volts r.m.s. and frequency range from 100 Hz to 10,000 Hz. The plots between Brightness(EL) and voltage for typical samples are shown in fig. 5.1 to 5.5. From these plots it is observed that the threshold voltage, ie. the voltage above which EL brightness starts, decreases with increase in the frequency and it varies between 250 volts to 500 volts (Table No.5.1). However, the variation ~~is~~ of thershold voltage with activator concentration is not systematic.

The EL brightness vs. applied voltage for a fixed frequency such a variation for different samples were plotted(fig. no.5.6 to 5.9)and it is observed from the plots after threshold voltage the brightness increases very rapid~~e~~ly.

The nature of possible relationship between brightness and applied voltage is studied by plotting

1) log (B/v) versus $\frac{1}{v}$
2) log (B/v) versus $1/\sqrt{v}$
3) log (B) versus v.
4) log B versus 1/v
5) log B versus $1/\sqrt{v}$.

Some typical plots between log B **versus** log V (Fig.5.20 and 5.21) for three typical frequencies viz. 100Hz, 500Hz and 1KHz are examined. A striking variation is observed for both the phosphors under study. Plots at 100Hz are non-linear and linearity goes on increasing with frequency. The plots assumes practically linear nature beyond certain voltage. Brightness saturation is however, is not observed in the range of voltage under study. The linearity of a plot between log B vs. log V suggests that the brightness and voltage follow power law relation of the form (14).

$$B = aV^n$$

at higher frequencies and higher voltage.

In above equation 'a' and 'n' being constants. The relation is similar to equation 5.11 with Vo = 0, similar relation is observed for CaS:Mn phosphor by Gour (15); Lawangar et al (27) for CaS:Bi:Pb phosphors and Patil M.G. (32) for CaS:Mg:Dy phosphors.

The plots of log B vs. $1000/\sqrt{v}$ has a linearily with two different slopes (fig. 5.18 and 5.19). The linearity is more clear at high frequency and lower voltage region. The observations seems to support power law relation more correctly for lower voltage and almost a power law holds good. Plots of log B vs. V are not exactly linear, however a careful study shows linearity for low voltages in both the phosphors. This suggest a possibility that at low voltage, brightness voltage follow exponential behaviour as such log B, vs. log V plots and log B vs. V plots studied together tend to a striking behaviour that brightness voltage seems to obey expoential relations at low voltage and power law relation for higher voltages. A careful study however to conform this is needed.

The plots between log $(\frac{B}{V})$ vs. $\frac{1}{V}$ and log $(\frac{B}{V})$ vs. $1/\sqrt{V}$. do not give a clear indication about brighthess-voltage relationship. (fig. 5.10 to 5.13). The knee structure of the plots at low frequencies around 500 volts observed in all the phosphor under study, is probabily indicative of a sort of phase transition which results into change in the behaviour of the phosphor.

### 5.3.2 Frequency dependance of EL-brightness

Brightness is found to be a function of voltage of applied voltage. Typical graphs between log B and log f are shown in fig. 5.22 and 5.23.

The observed results from the graphs are summarised as at low frequency the brightness increases almost linearly. The frequency range over which the linear relationshiph holds depends upon the exciting voltage. At higher voltages brightness increases more rapidly than at lower voltages. At moderately higher frequencies the brightness finally saturates. This said behaviour can be understood on the basis of a relation proposed by Thornton (35), Viz. B = No. f (1- exp. (A/F). Here A is function of voltage which increases with increase of applied voltage. At low voltage the deplection of ionised activators does not occur during the cycle even at low frequency and No is expected to be independent of frequency. At higher voltages, however, the deplection of ionised activator is strong and No varies as square root of applied frequency, and therefore, the slope of the curve increases at higher voltages.

### 5.3.3 Brightness Waves

Typical brightness wave pattern obtained by varying either the voltage or the frequency, as shown in photograph fig. (5.24). According to Waymouth and Britter (40) the light emission from a single grain is concentrated in certain small spots and these spots emitt brightness waves.

### 5.3.4 Mechanism of Electroluminescence

To observe EL emission high fields are required for all samples studied, the threshold voltages found to be greater than 250 volts rms. The requirement of an intense electric field for emission, along with the existance of power law relationship between brightness and voltage suggests that the probable mechanism of EL in these phosphors, is likely to be the direct field conisation of either valence band electrons or impurity centres, where the transfer of electrons in to the conduction band takes place by quantum mechanical tunneling process ( 15, 33).

Kinetics involved in the EL process in the present study, the existance of power law relationship between brightness and voltage indicates the bimolecular process in recombination of electrons with luminescence centres (14), Moreover, variation of brightness with frequency as per equation given by D.Curie (5.16) also points the bimolecular process.

Table No. 5.1 : - Values of Threshold voltages for different samples for different frequencies.

| Sample no. | Frequency in Hz<br>100 Hz | 500Hz | 1KHZ | 3 KHZ |
|---|---|---|---|---|
| MD-21 | 300 | 400 | 448 | 450 |
| MD-25 | 300 | 425 | 425 | 425 |
| MD-29 | 250 | 406 | 375 | 440 |
| MD-33 | 200 | 330 | 325 | 355 |
| MD-34 | -- | 800 | 250 | 500 |
| MD-36 | 250 | 325 | 340 | 360 |
| MD-39 | 285 | 320 | 330 | 340 |
| MD-40 | 280 | 360 | 336 | 380 |
| MD-41 | 315 | 460 | 480 | 470 |

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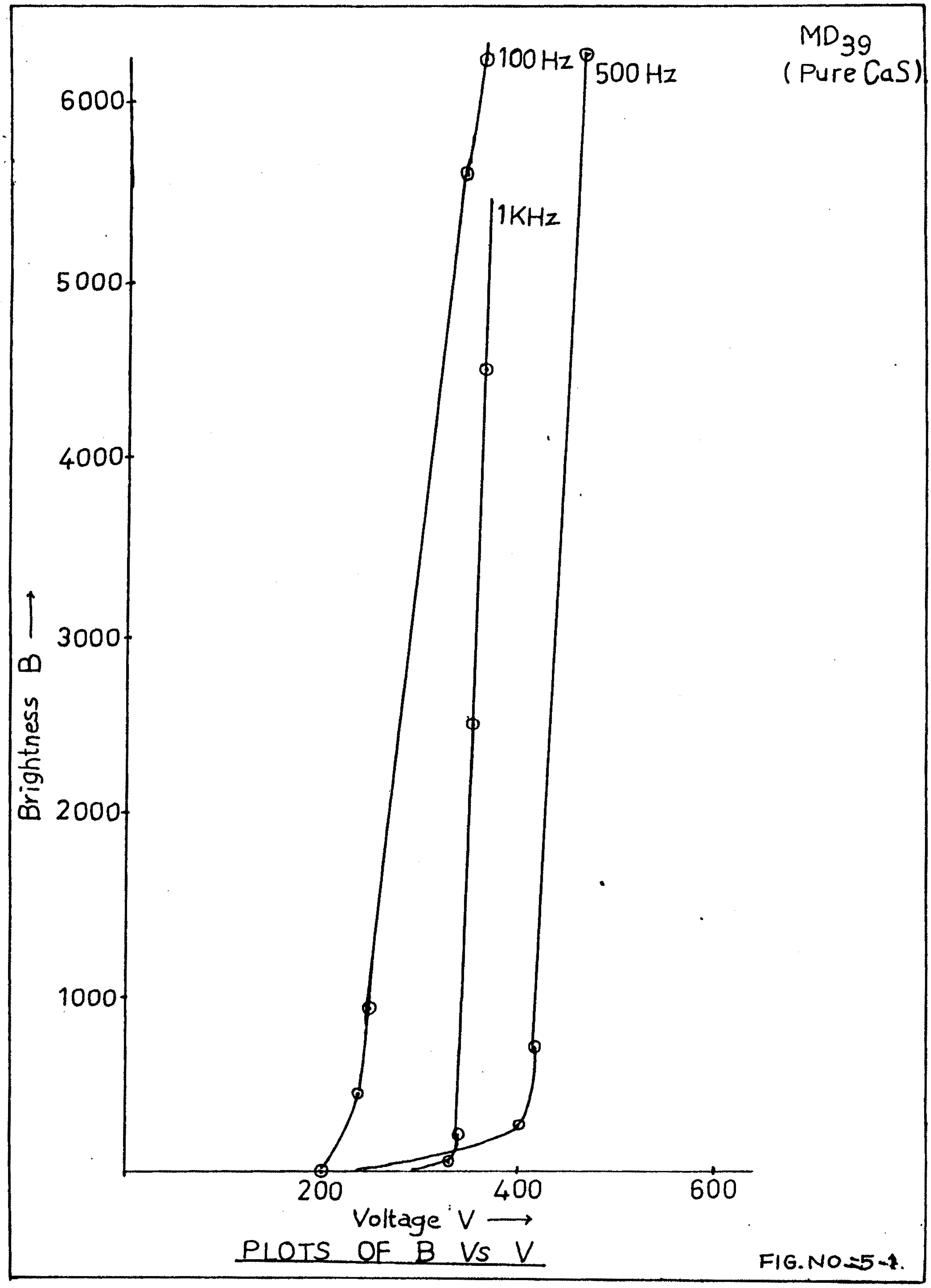
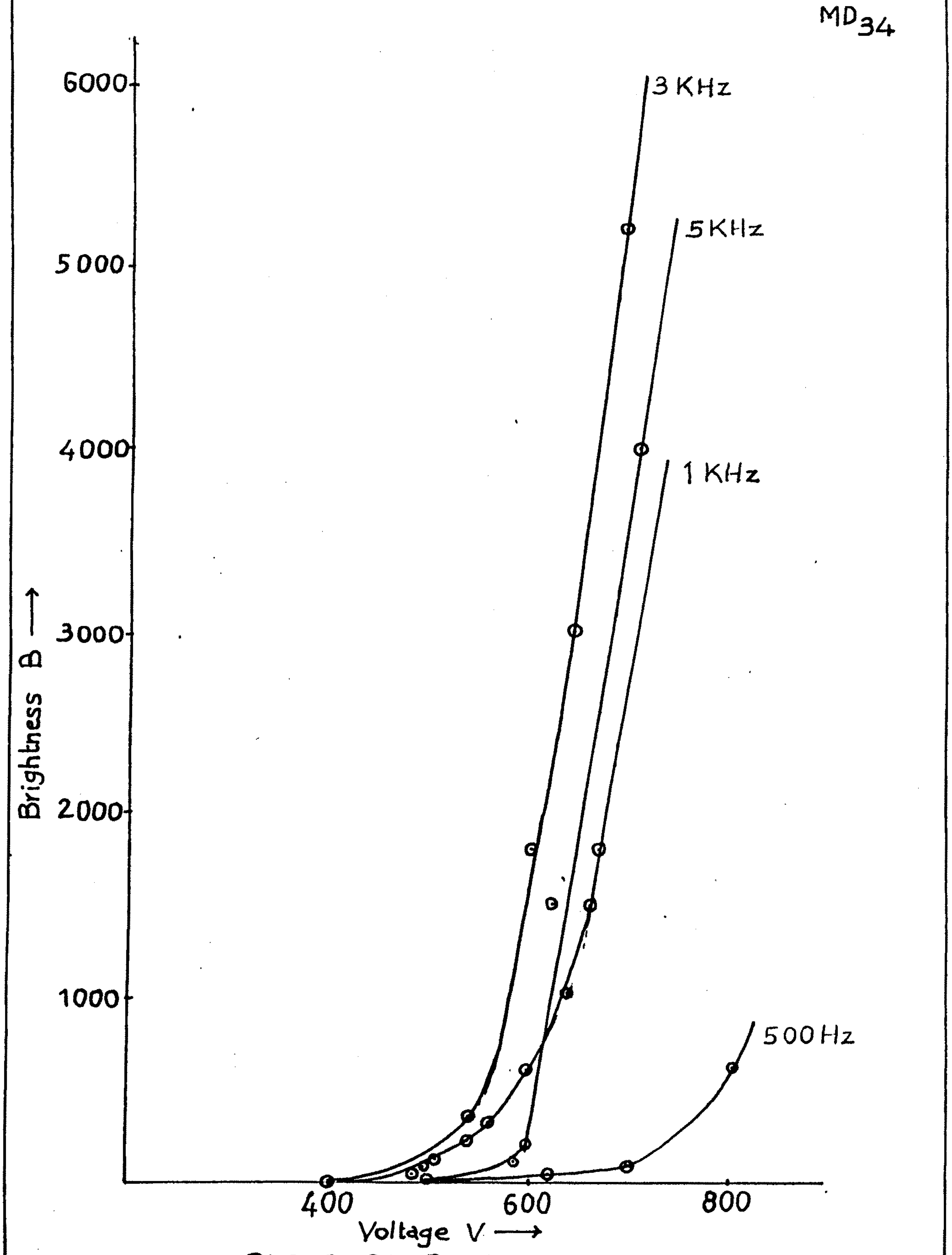


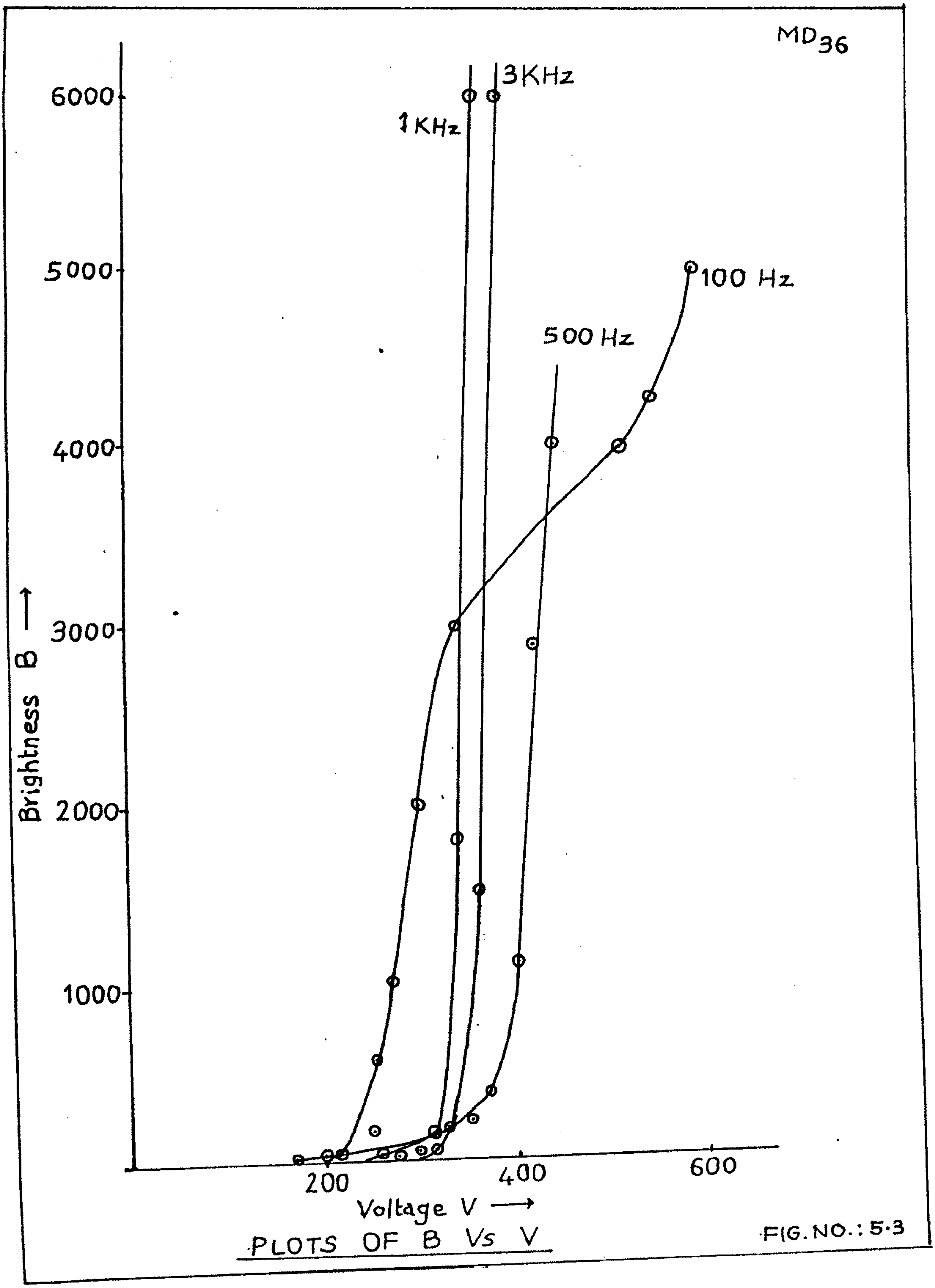
PLOTS OF B Vs V

FIG. NO=5-1.



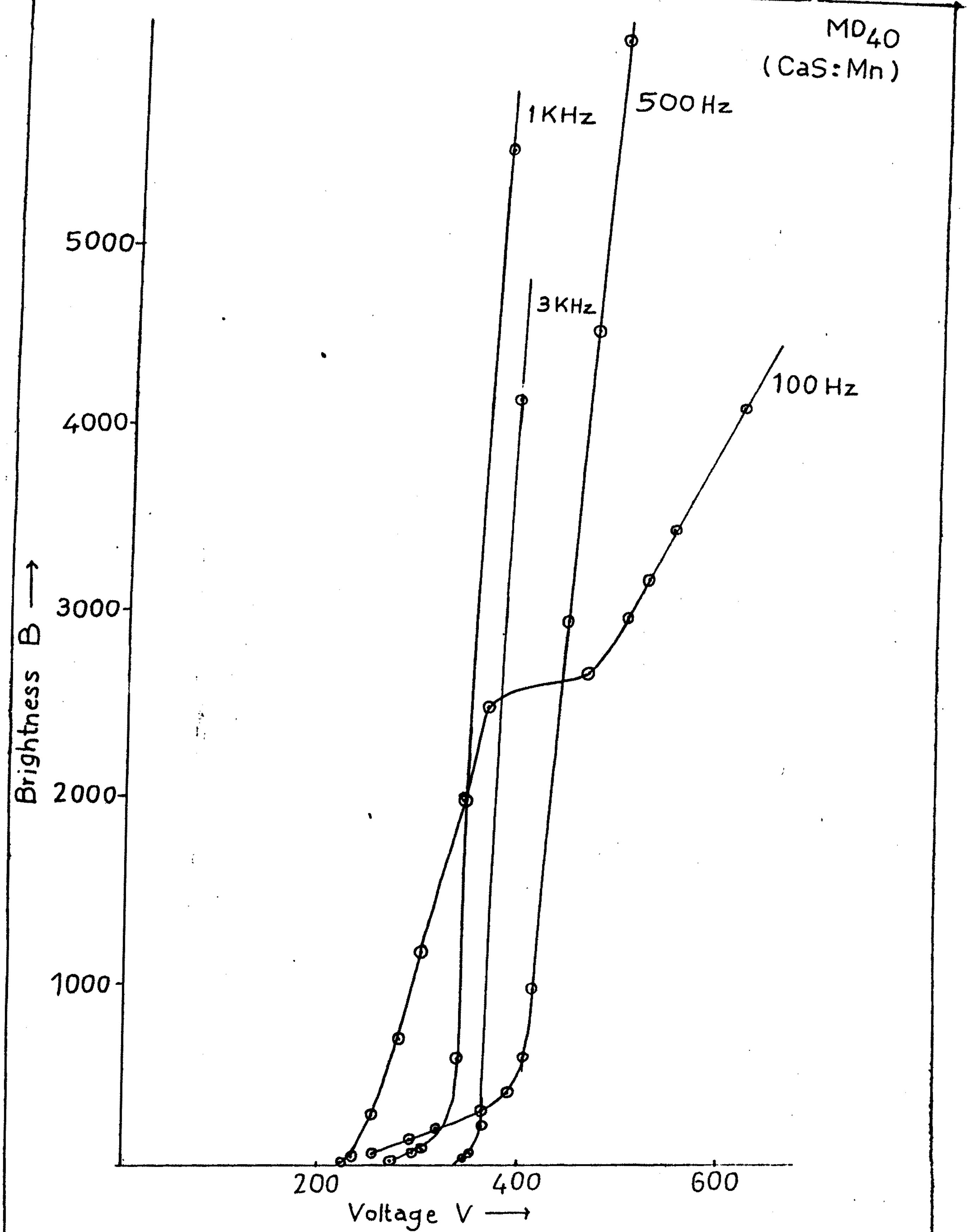
PLOTS OF B Vs V

FIG. NO.: 5·2



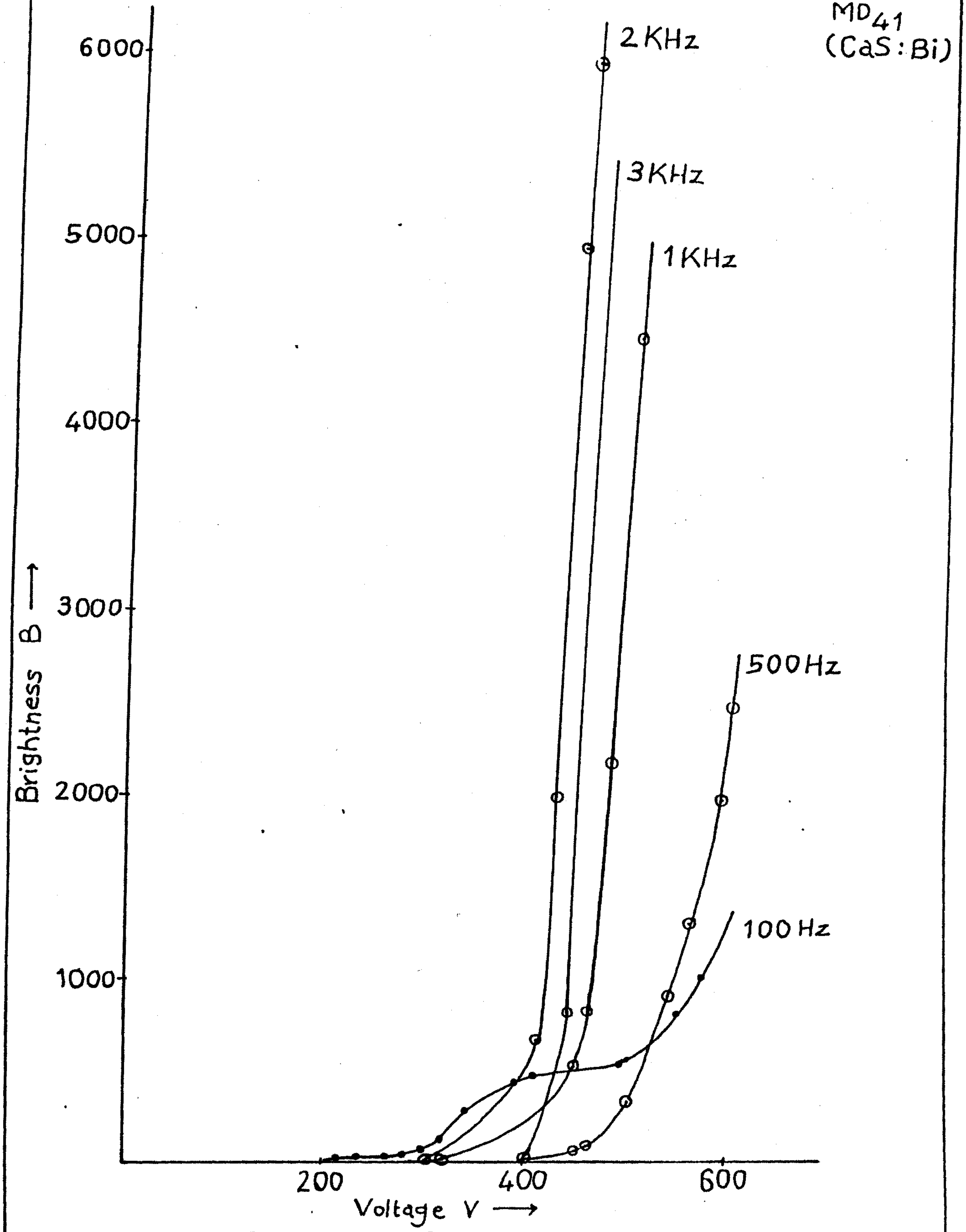
PLOTS OF B Vs V

FIG. NO.: 5·3



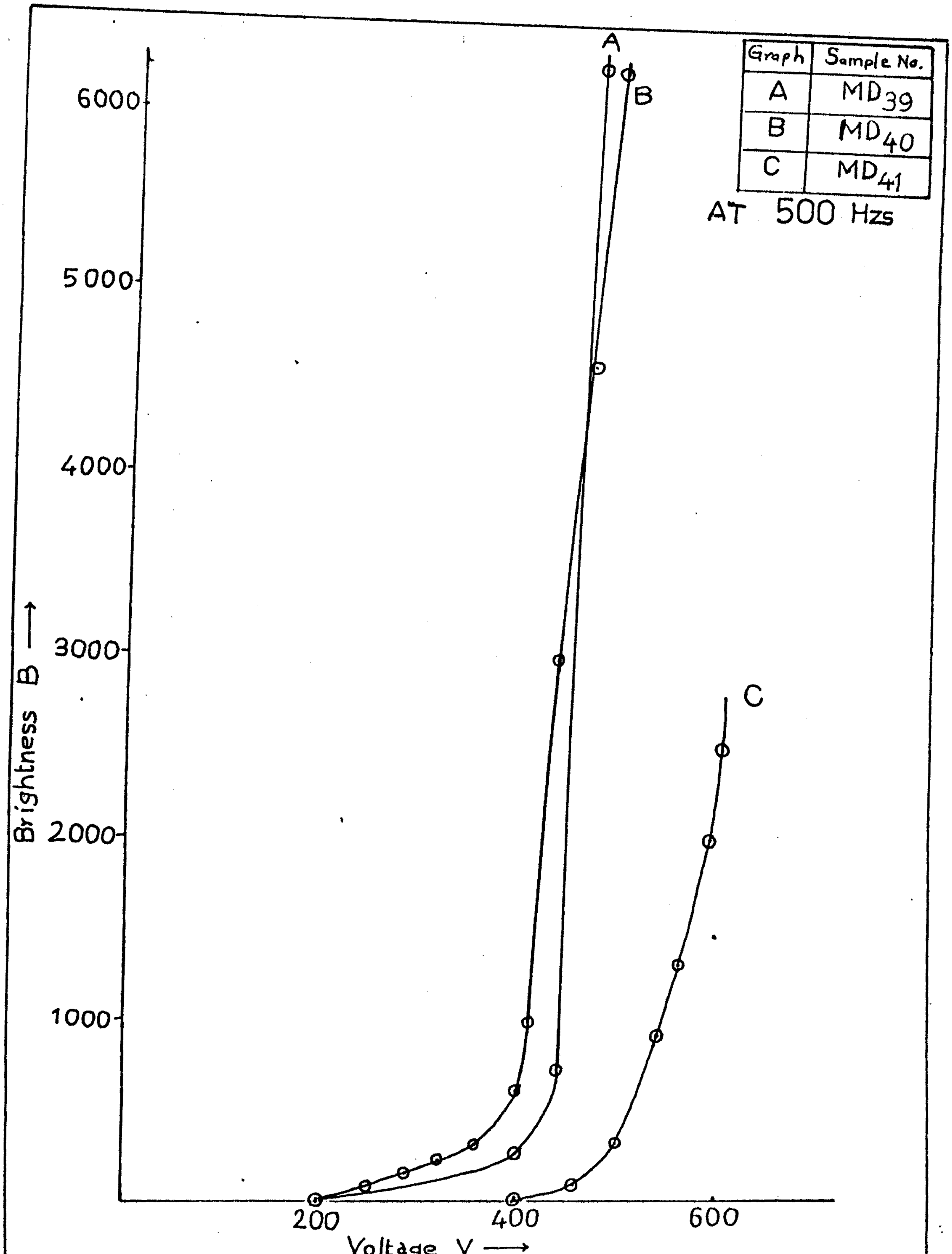
PLOTS OF B Vs V

FIG.NO.:5·4.



PLOTS OF B Vs V

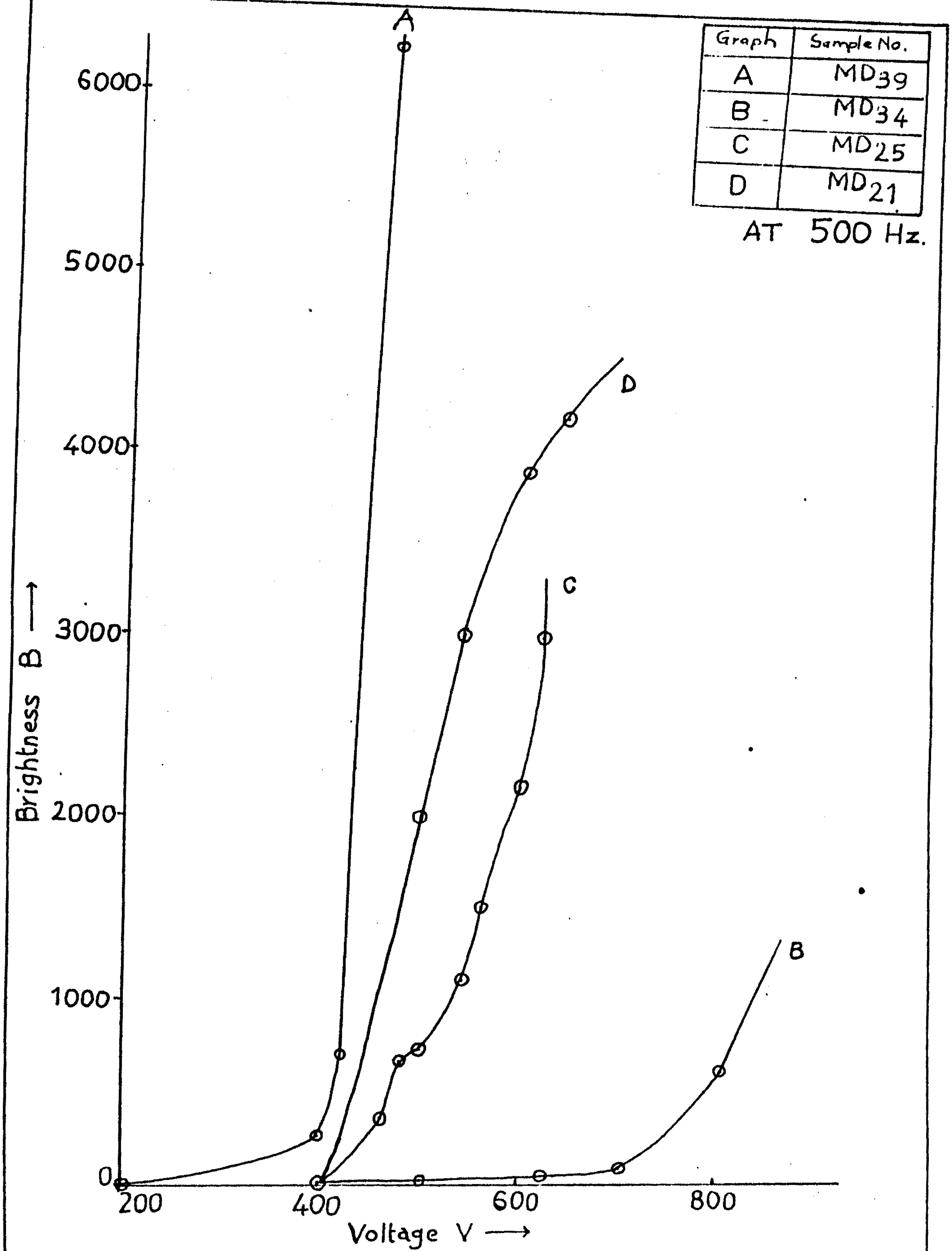
FIG. NO.: 5·5



| Graph | Sample No. |
|---|---|
| A | $MD_{39}$ |
| B | $MD_{40}$ |
| C | $MD_{41}$ |

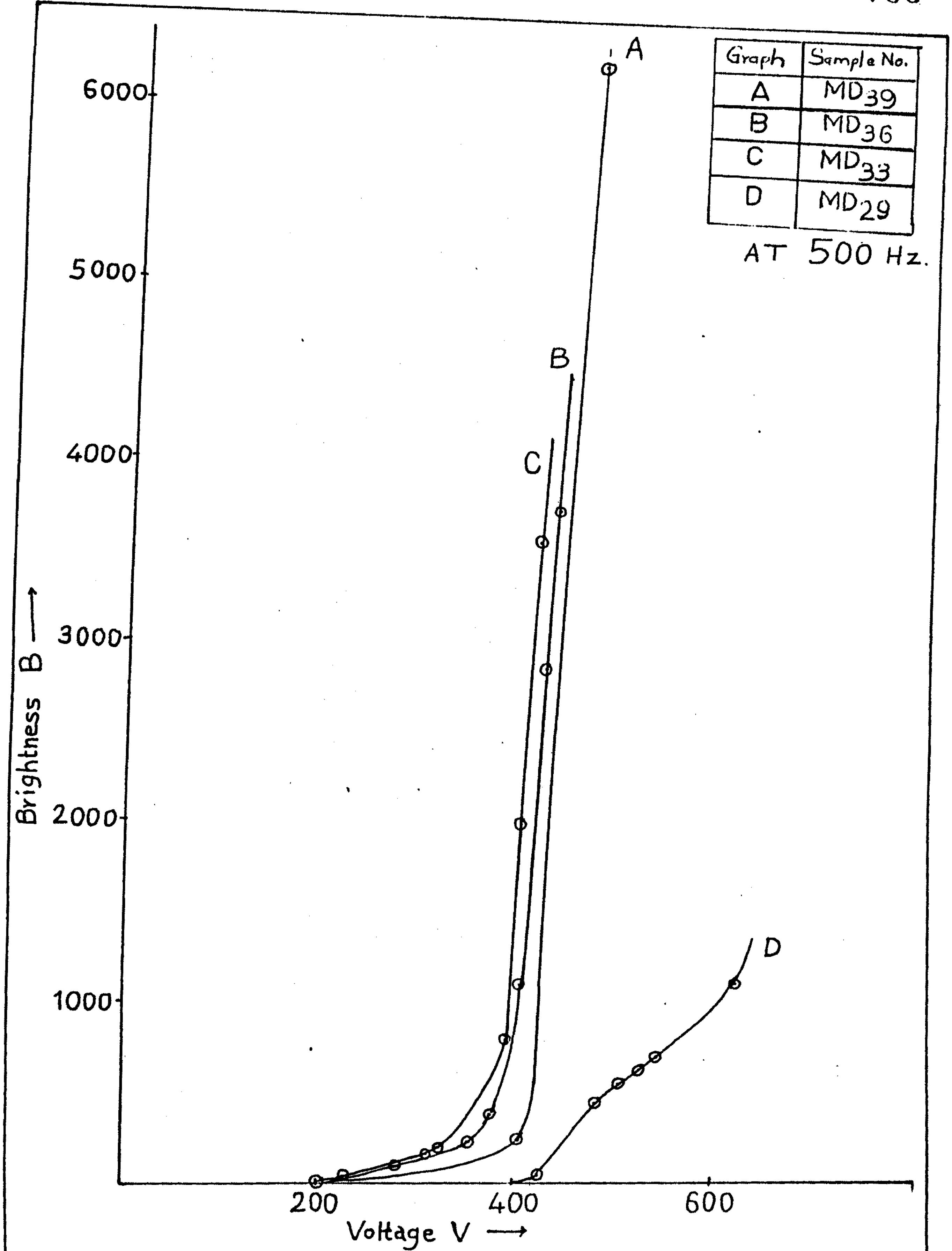
PLOTS OF B Vs V

FIG. NO.: 5·6.



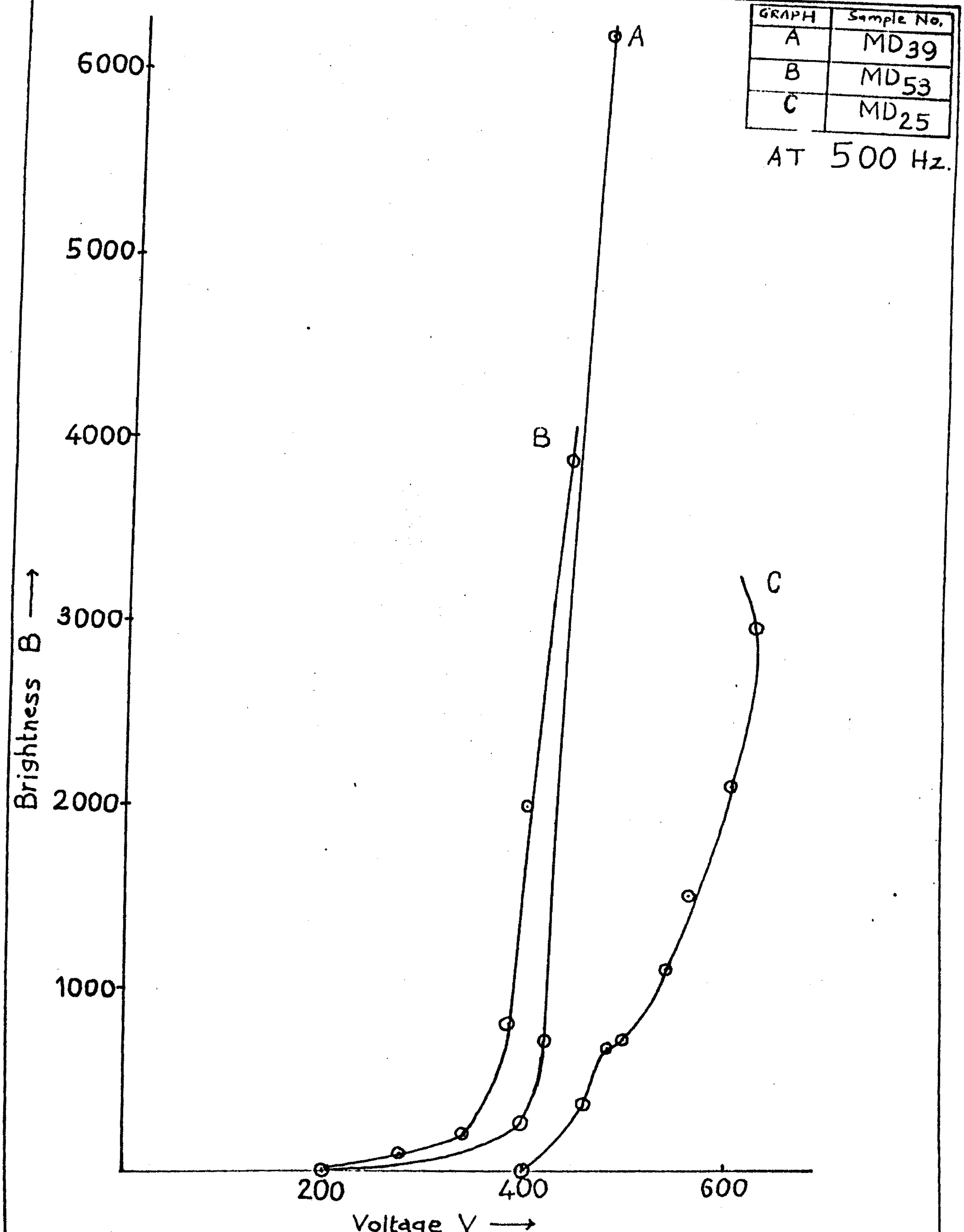
PLOTS OF B Vs V

FIG.NO.5·7.



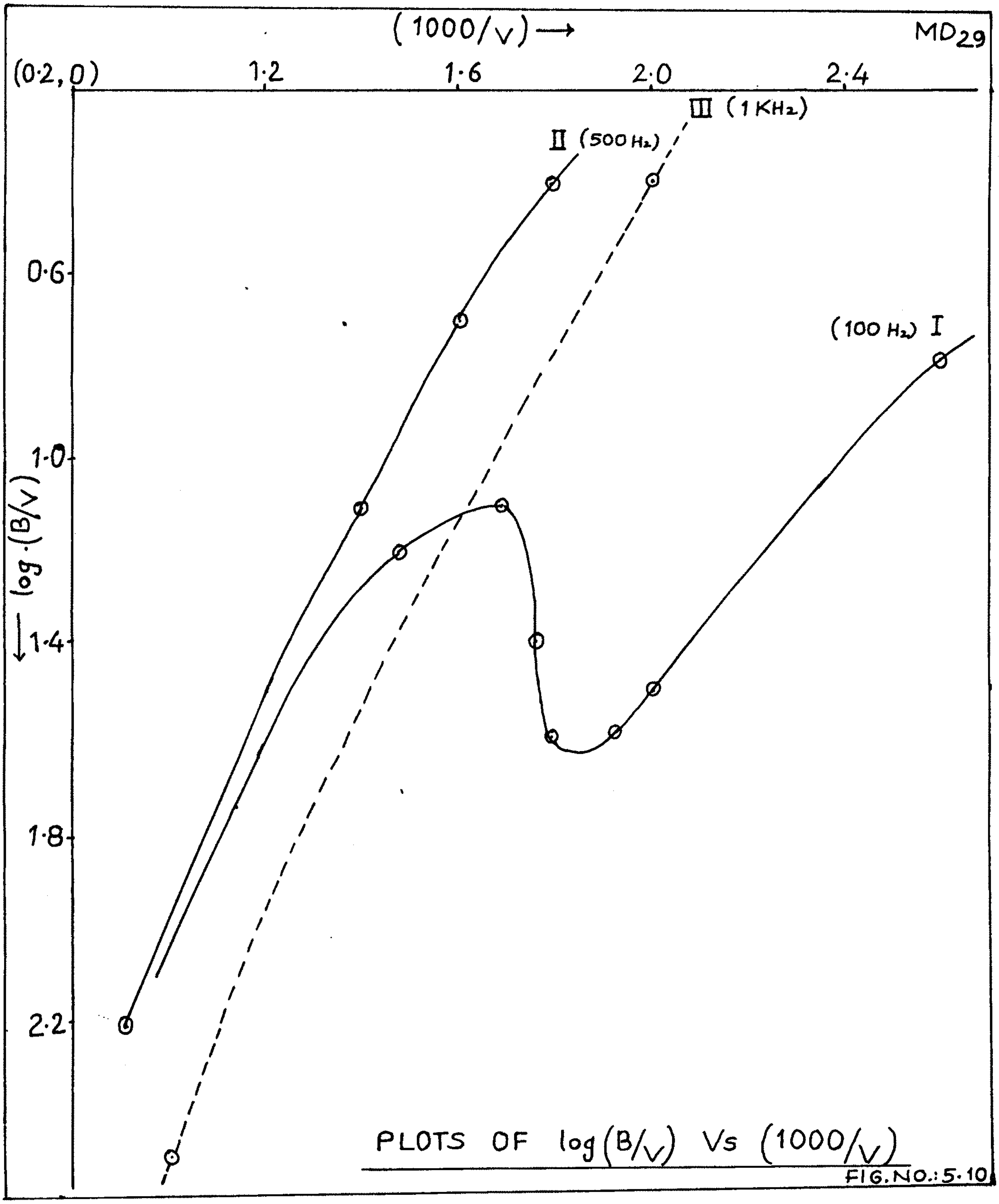
PLOTS OF B Vs V

FIG. NO.5.8.



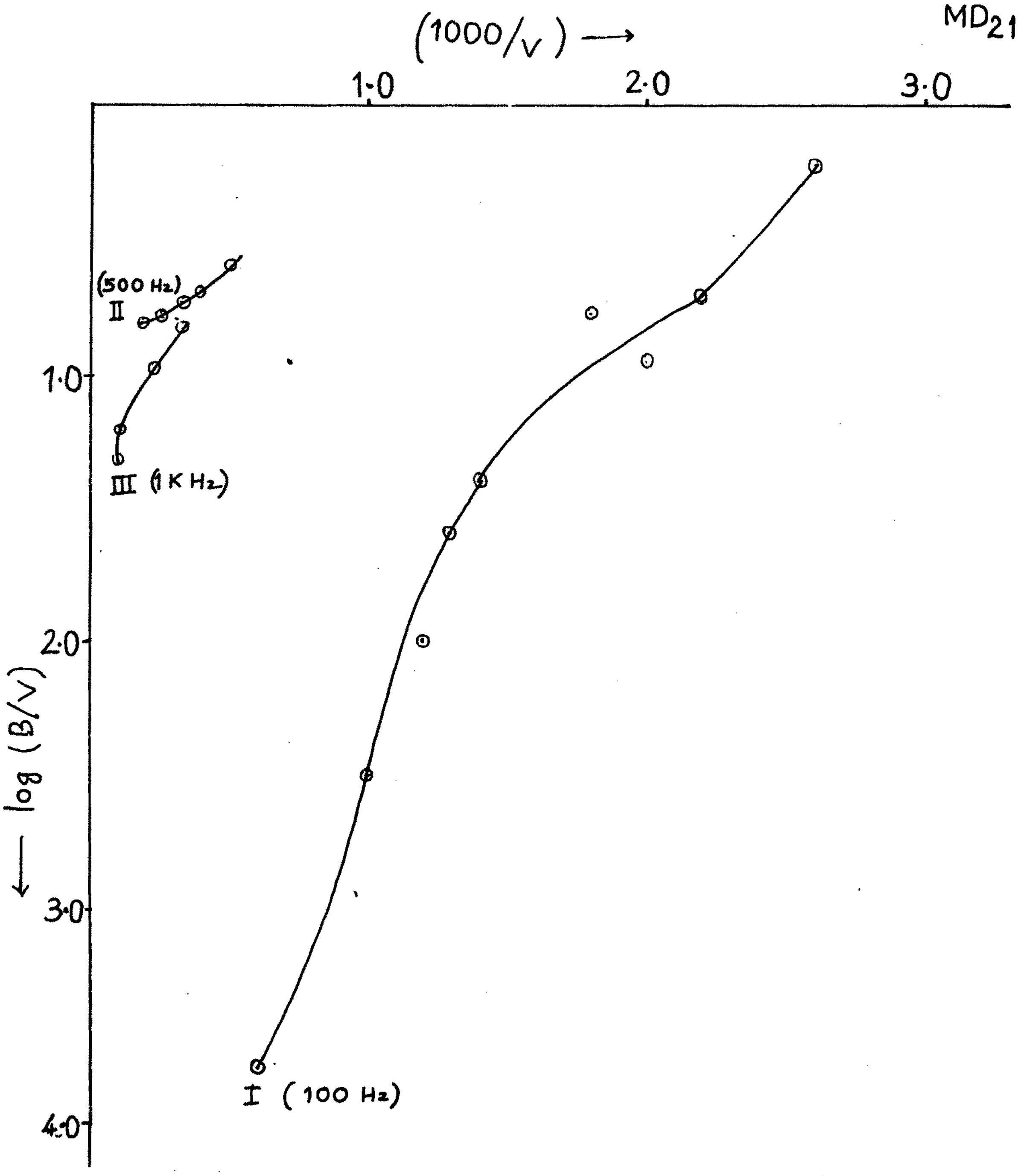
PLOTS OF B Vs V

FIG. NO.: 5·9



PLOTS OF log(B/V) Vs (1000/V)

FIG. NO.: 5·10



PLOTS OF log(B/V) Vs (1000/V)

FIG. NO. 5.11.

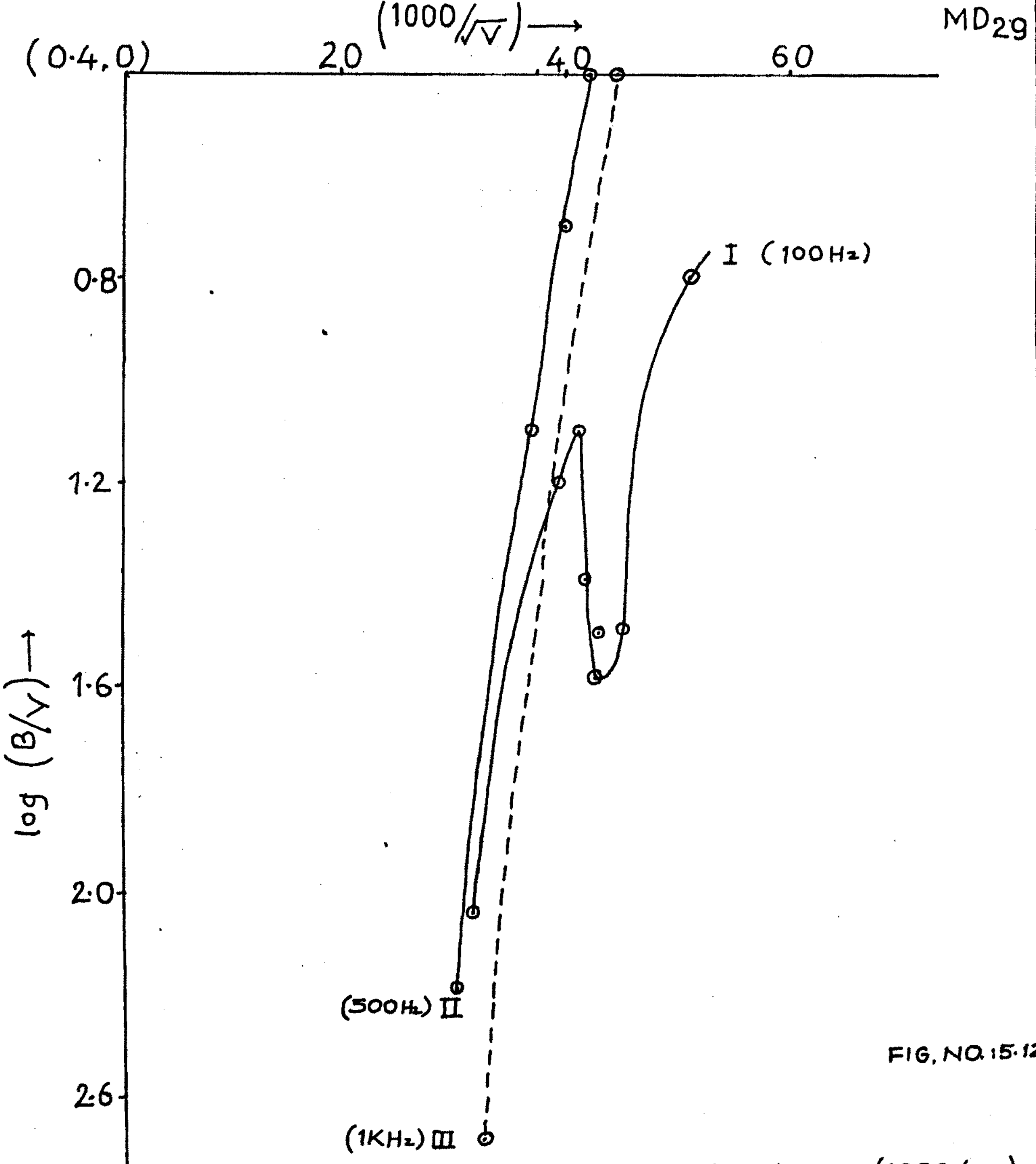
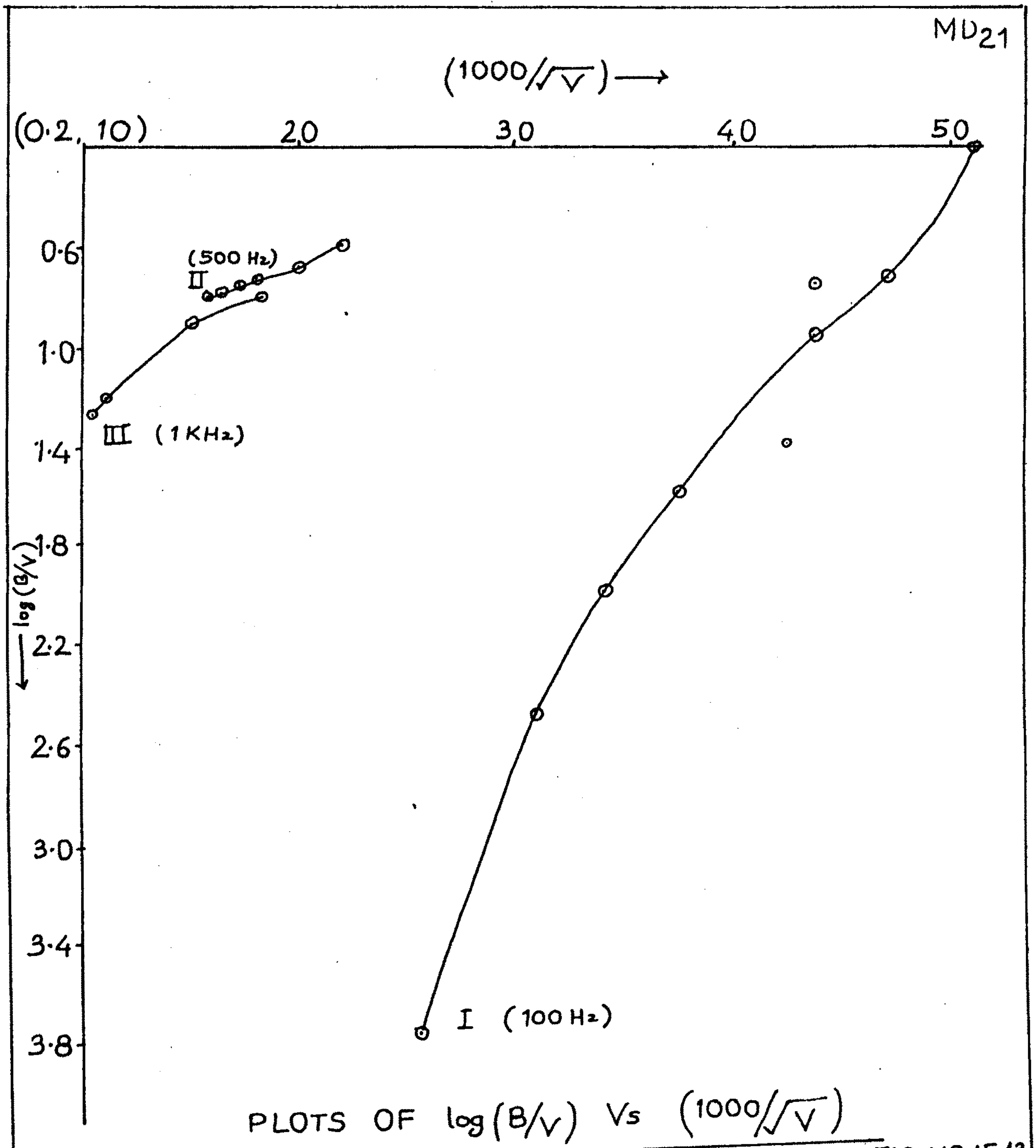


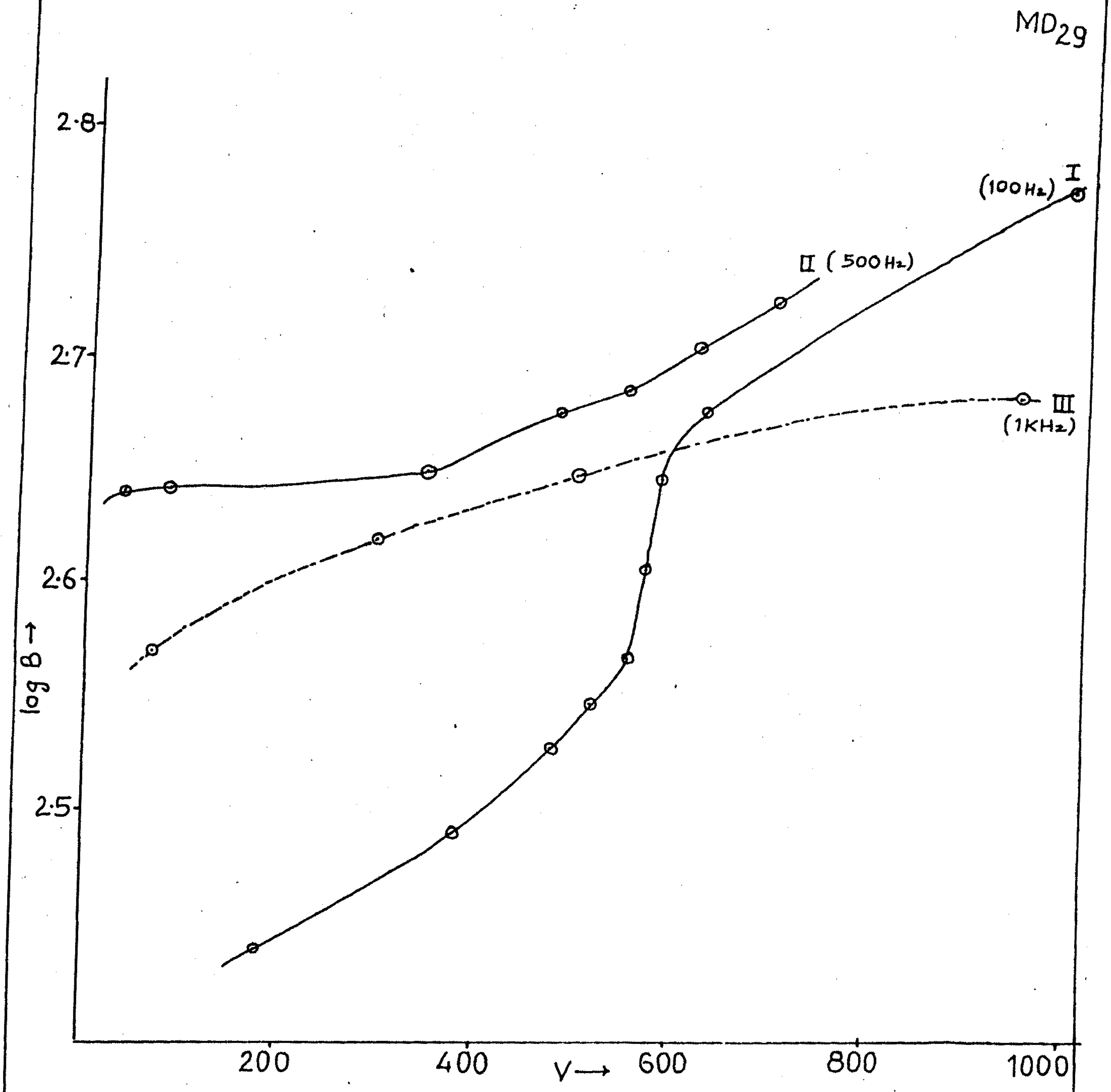
FIG. NO. 15·12

PLOTS OF (B/V) Vs (1000/√V)



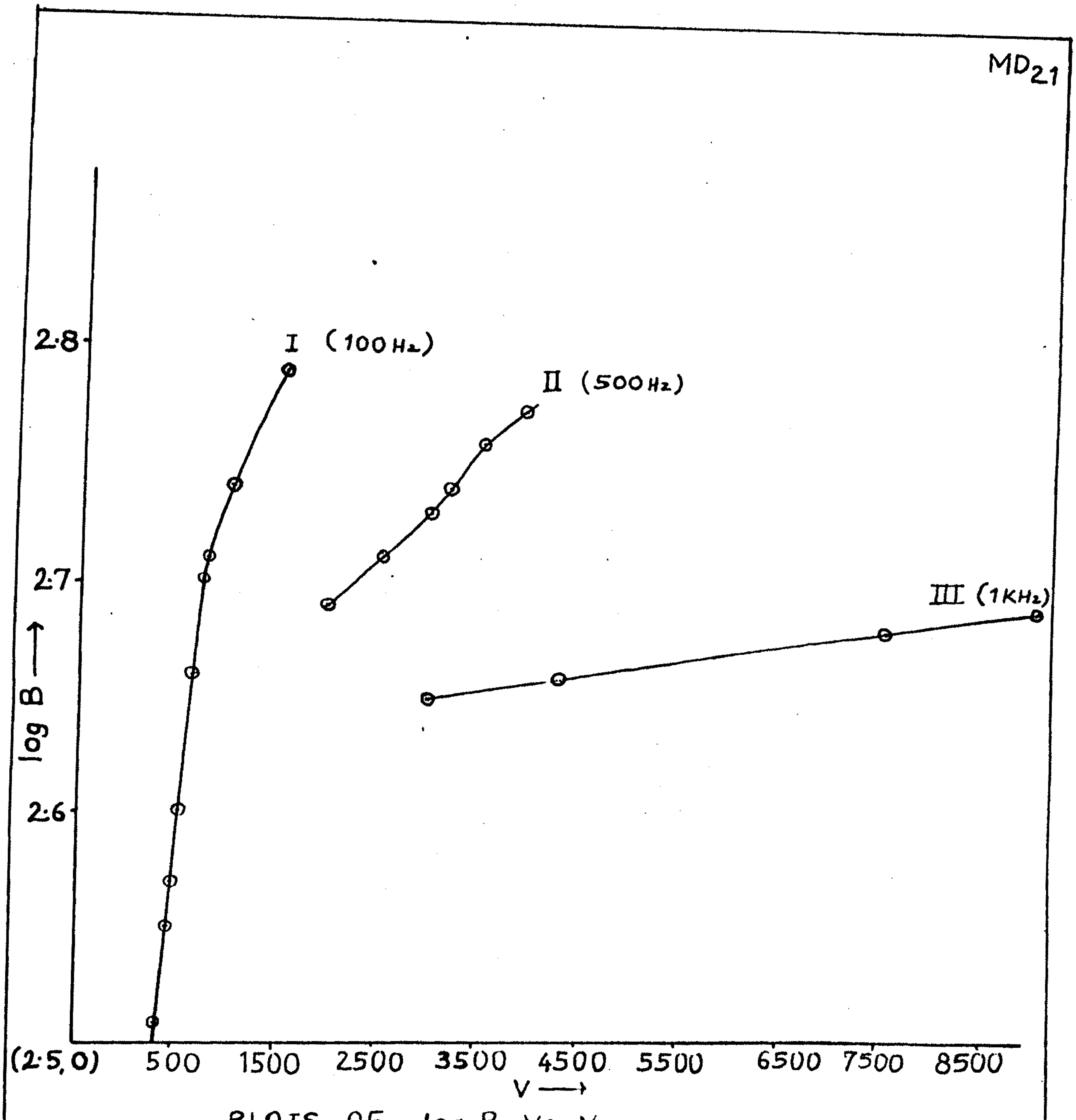
PLOTS OF log(B/V) Vs (1000/√V)

FIG. NO. 5·13



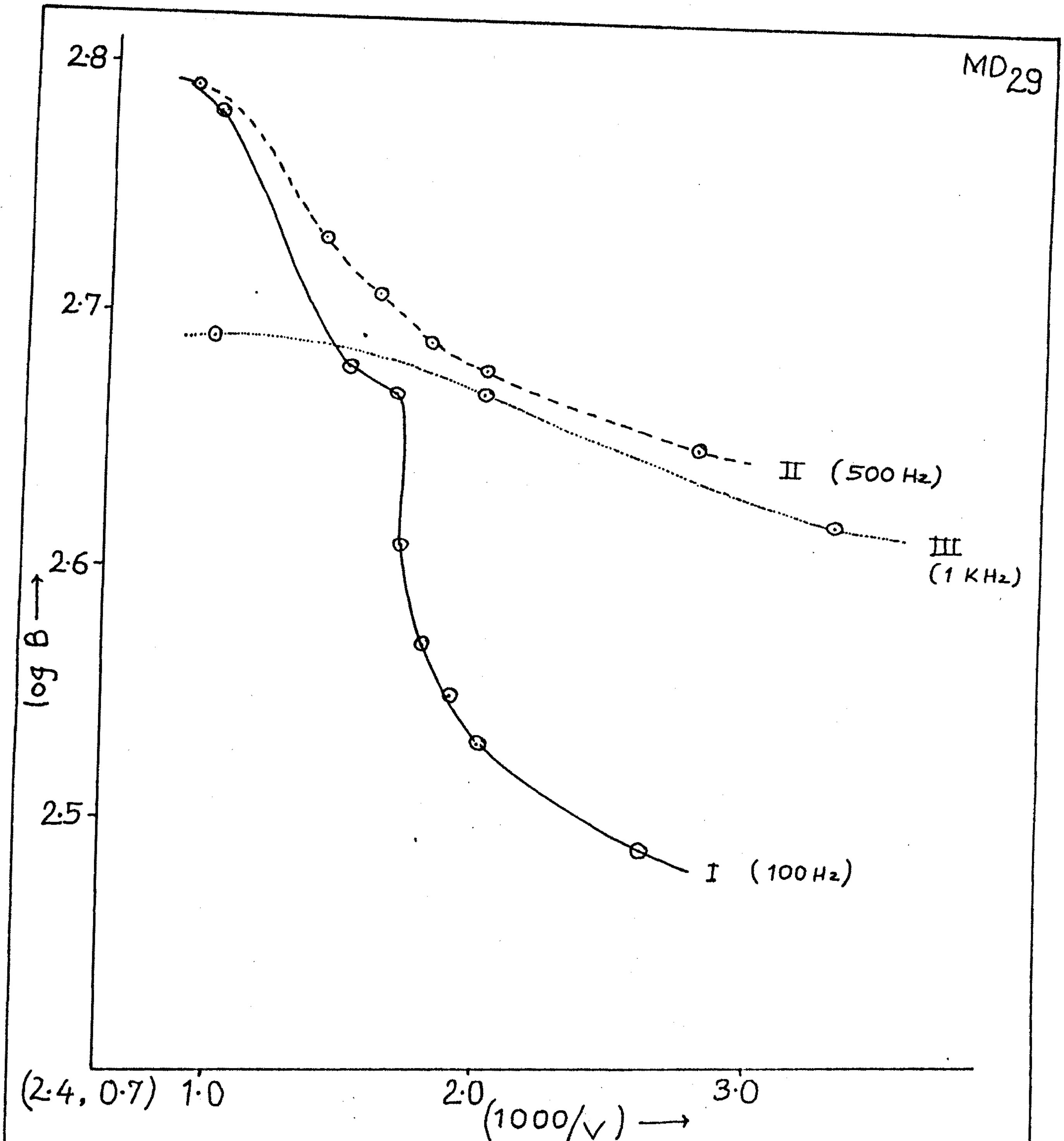
PLOTS OF log B Vs V

FIG. NO.: 5·14



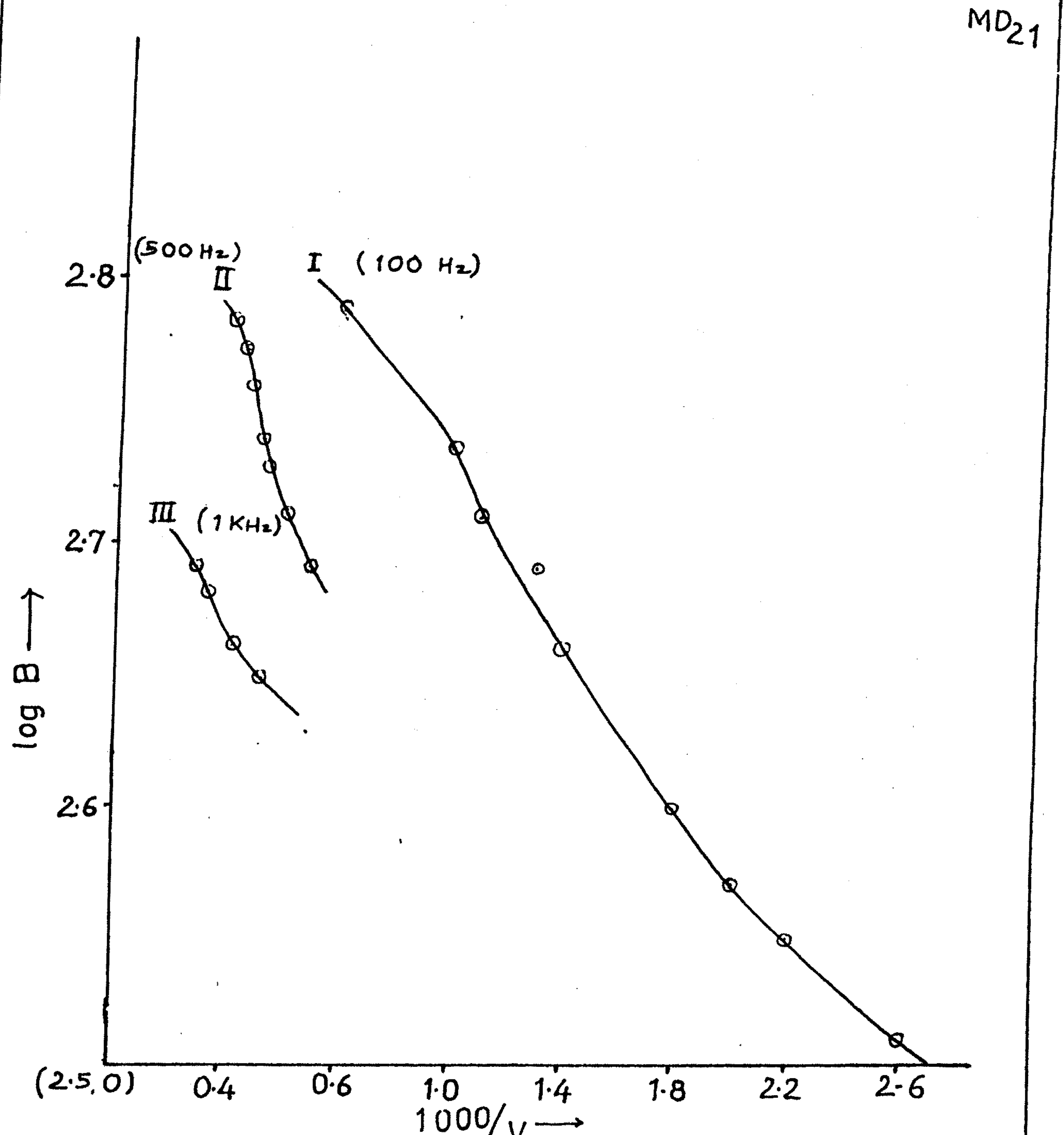
PLOTS OF log B Vs V

FIG. NO. 5·15.



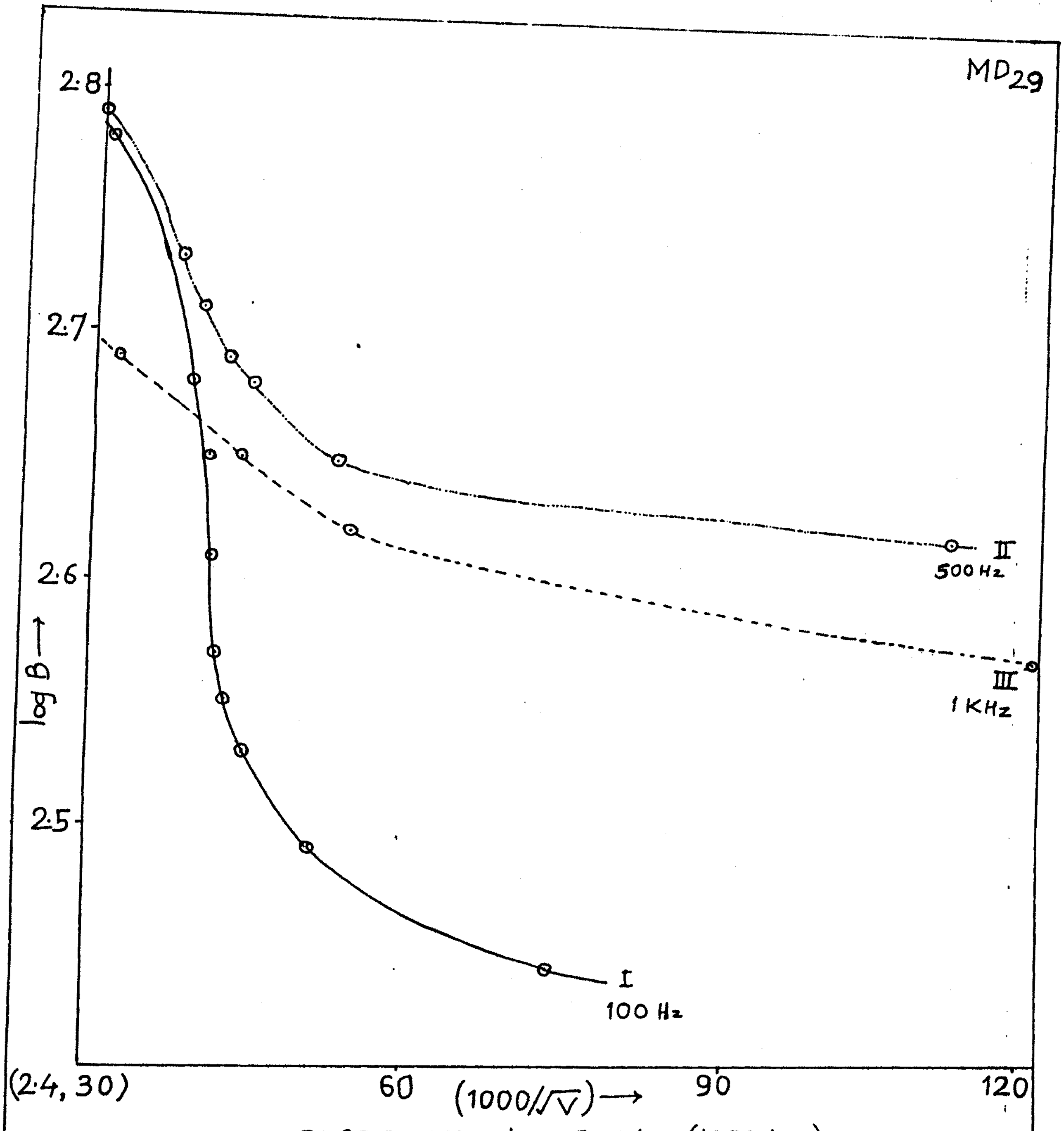
PLOTS OF log B Vs (1000/V)

FIG. NO:5·16



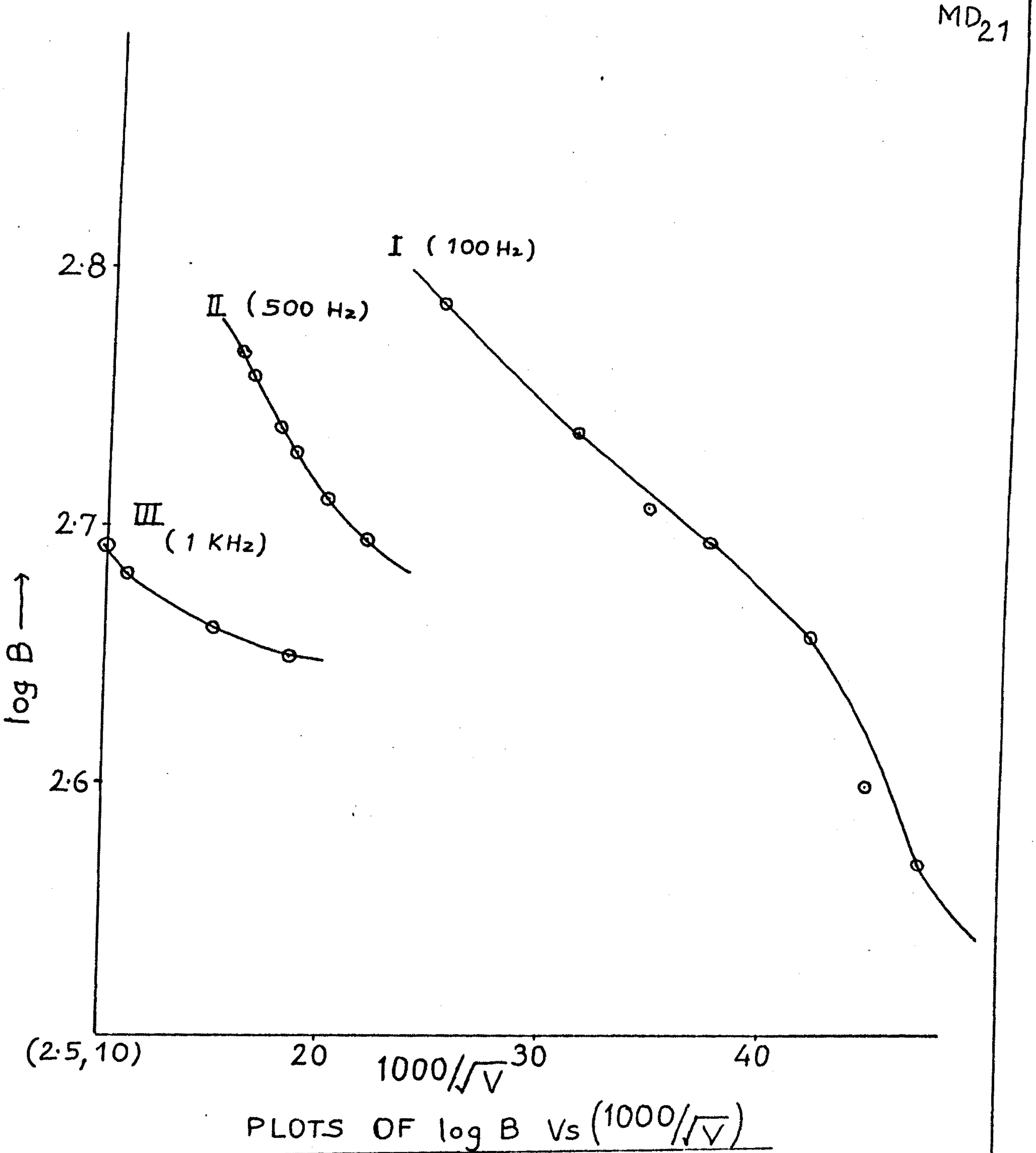
PLOTS OF log B Vs (1000/V)

FIG. NO: 5.17.



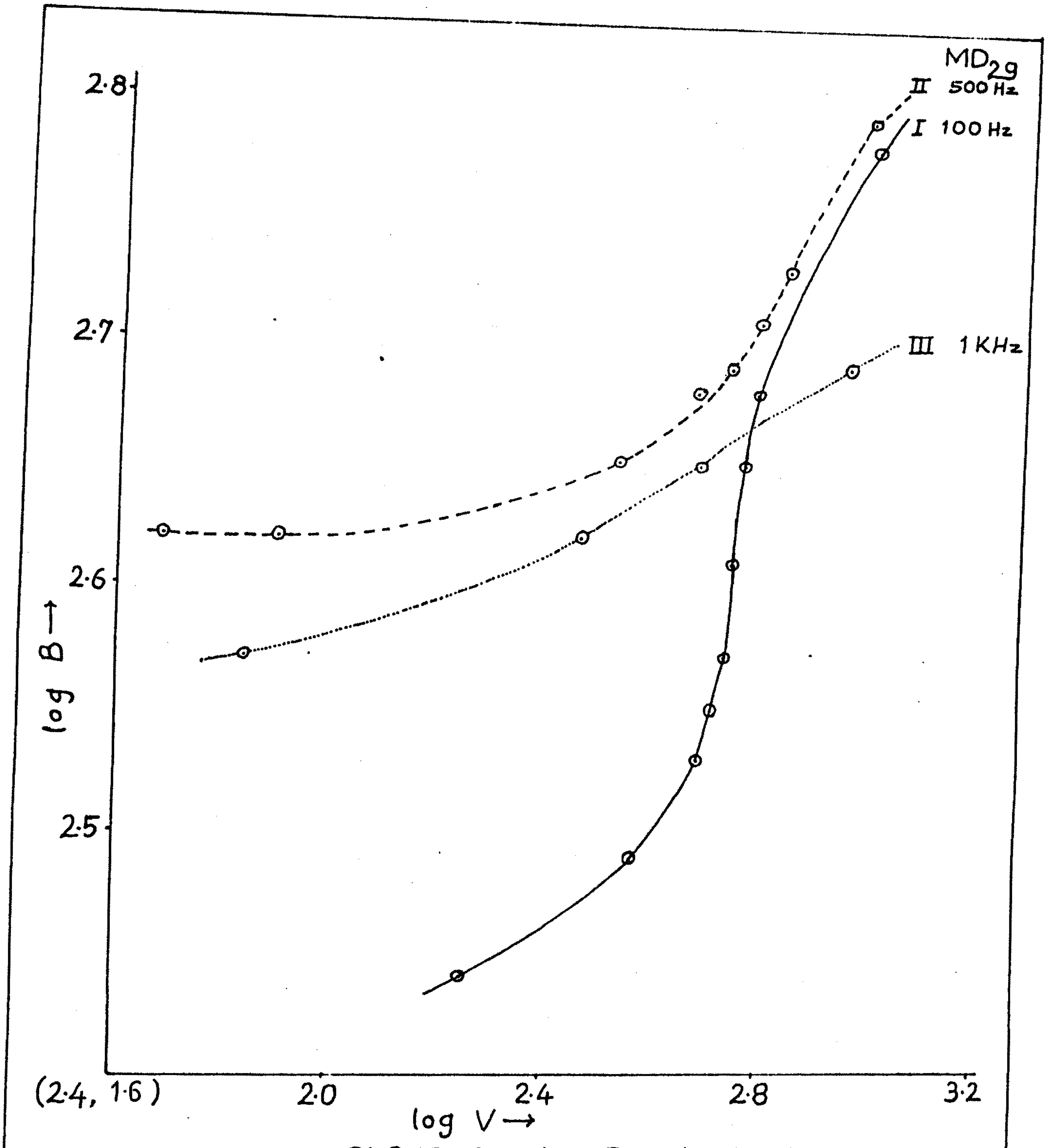
PLOTS OF log B Vs (1000/√V)

FIG. NO.: 5·18.

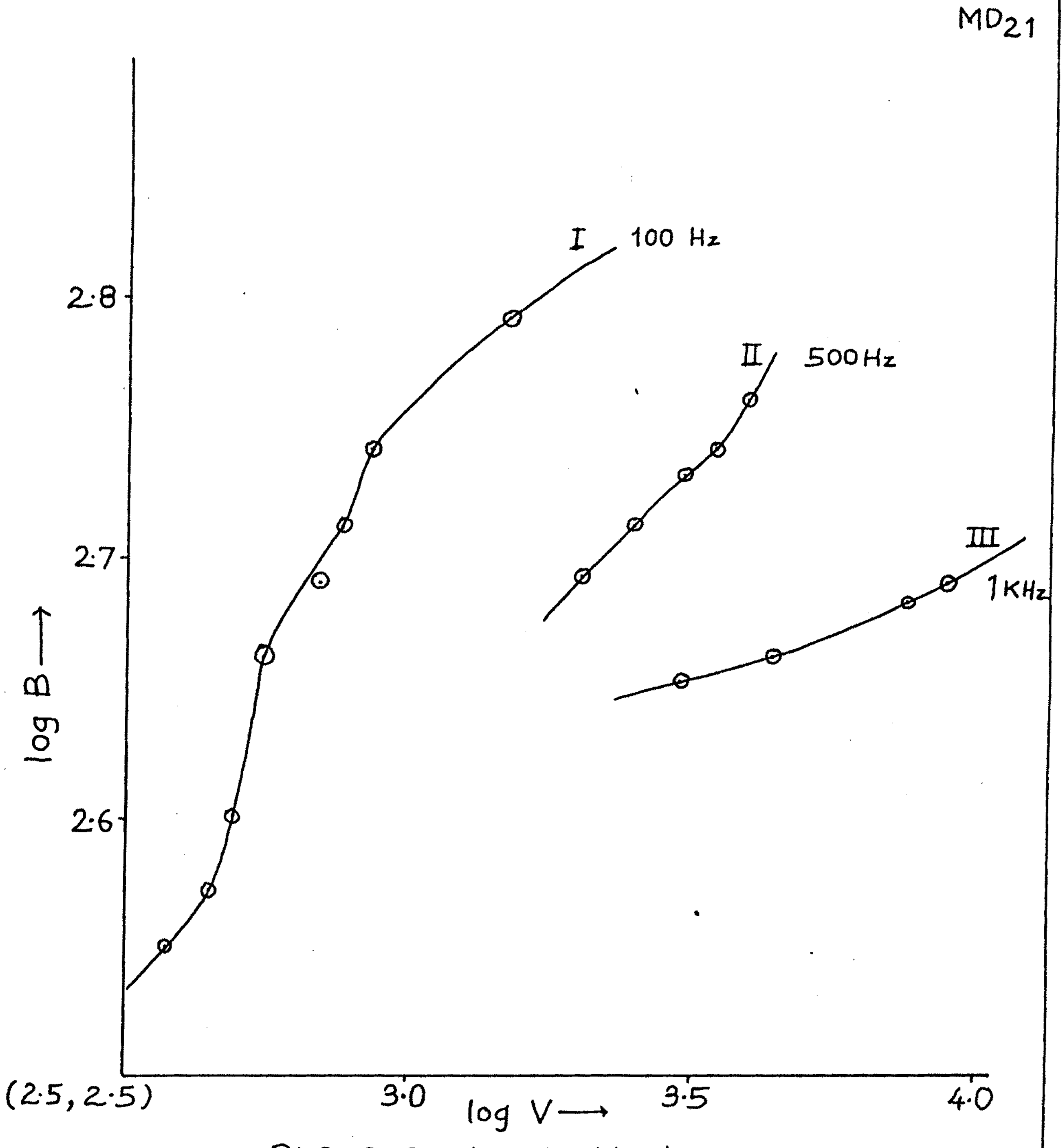


PLOTS OF log B Vs (1000/√V)

FIG. NO.: 5·19.

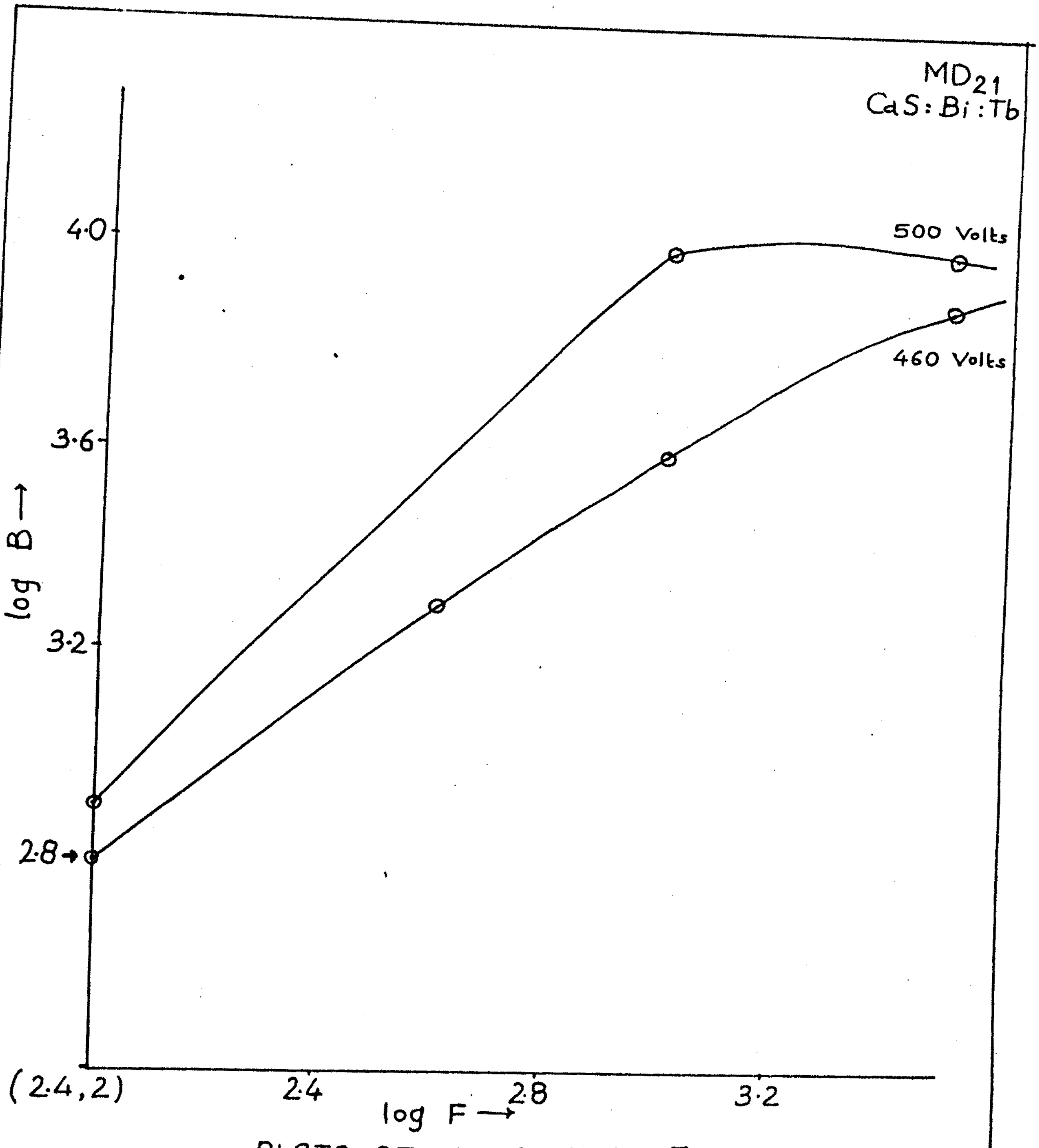


PLOTS OF log B Vs log V FIG. NO.: 5·20



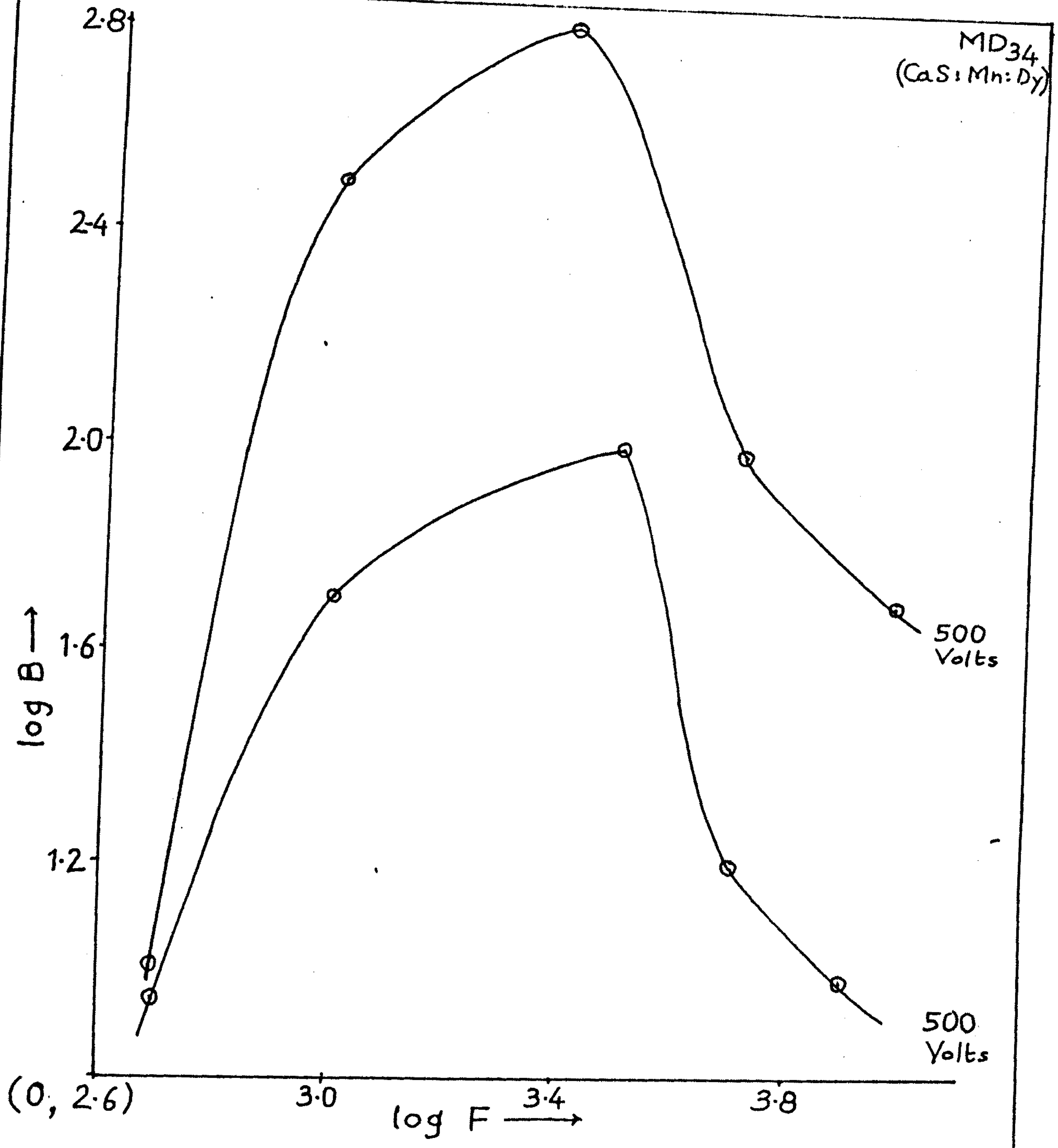
PLOTS OF log B Vs log V

FIG. NO.: 5·21.



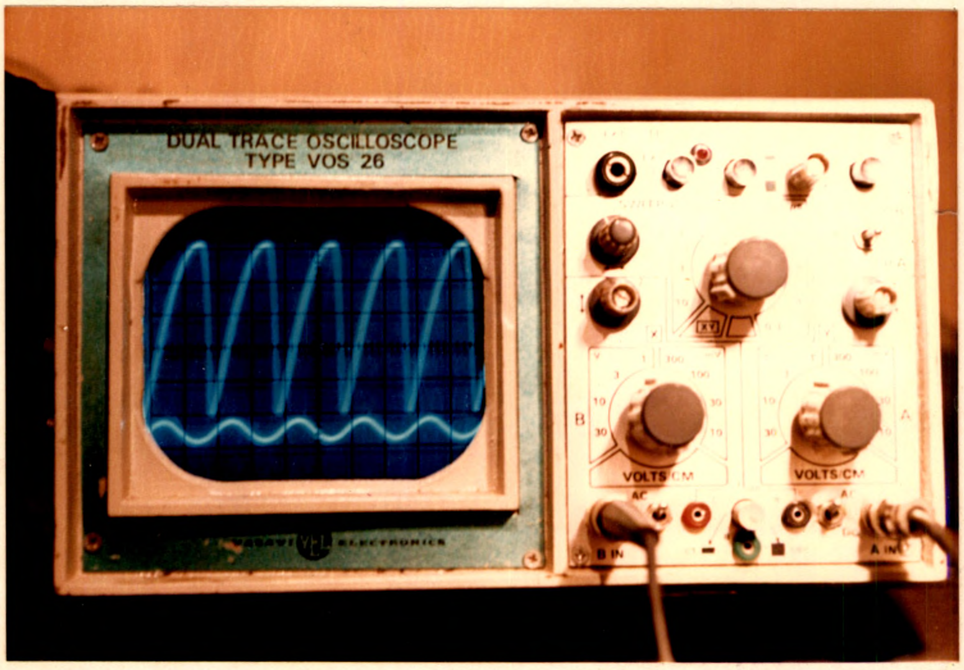
PLOTS OF log B Vs log F

FIG. NO.: 5.22



PLOTS OF log B Vs log F

FIG. NO.:5·23.



BRIGHTNESS WAVES (Fig No. 5·24)